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PHOTOCYCLIZATION OF SUBSTITUTED α-(*O*-ETHYLPHENYL)ACTETOPHENONES AND α-(*O*-TOLYL)ACETOPHENONES

presented by

Linging Wang

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of the requirements for the

Master of Science	degree in	Department of Chemistry

Major Professor's Signature

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Date

PHOTOCYCLIZATION OF SUBSTITUTED α-(*O*-ETHYLPHENYL)-ACETOPHENONES AND α-(*O*-TOLYL)ACETOPHENONES

By

Lingling Wang

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Abstract

PHOTOCYCLIZATION OF SUBSTITUTED
α-(*O*-ETHYLPHENYL)-ACETOPHENONES AND
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By

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The photochemistry of several substituted α-arylacetophenones was investigated. These ketones undergo intramolecular δ-hydrogen abstraction to form 1, 5 biradicals, which upon cyclization form indanols as photoproducts.

The intramolecular OH-to-benzene ring hydrogen bonding in the preferred conformation of such 1,5 biradical intermediate effects the photochemical behavior of these ketones. Tuning up the strength of such intramolecular hydrogen bonding is achieved by putting different ring substituents on the benzene ring. It turns out that an electron-donating methoxy group increases the product diastereoselectivity of the substituted α-(o-ethylphenyl) acetophenone by strengthening the above-mentioned hydrogen-bonding in reaction intermediate, while an electron-withdrawing cyanide group has exactly the opposite effect on diastereoselectivity. Temperature also effects product diastereoselectivity of these ketones.

Substituent also has an effect on steady-state photokinetics of α-arylacetophenones. The electron-donating methoxy group tends to increase the quantum yield and fasten the hydrogen abstraction while electron-withdrawing cyanide group has the opposite effects.

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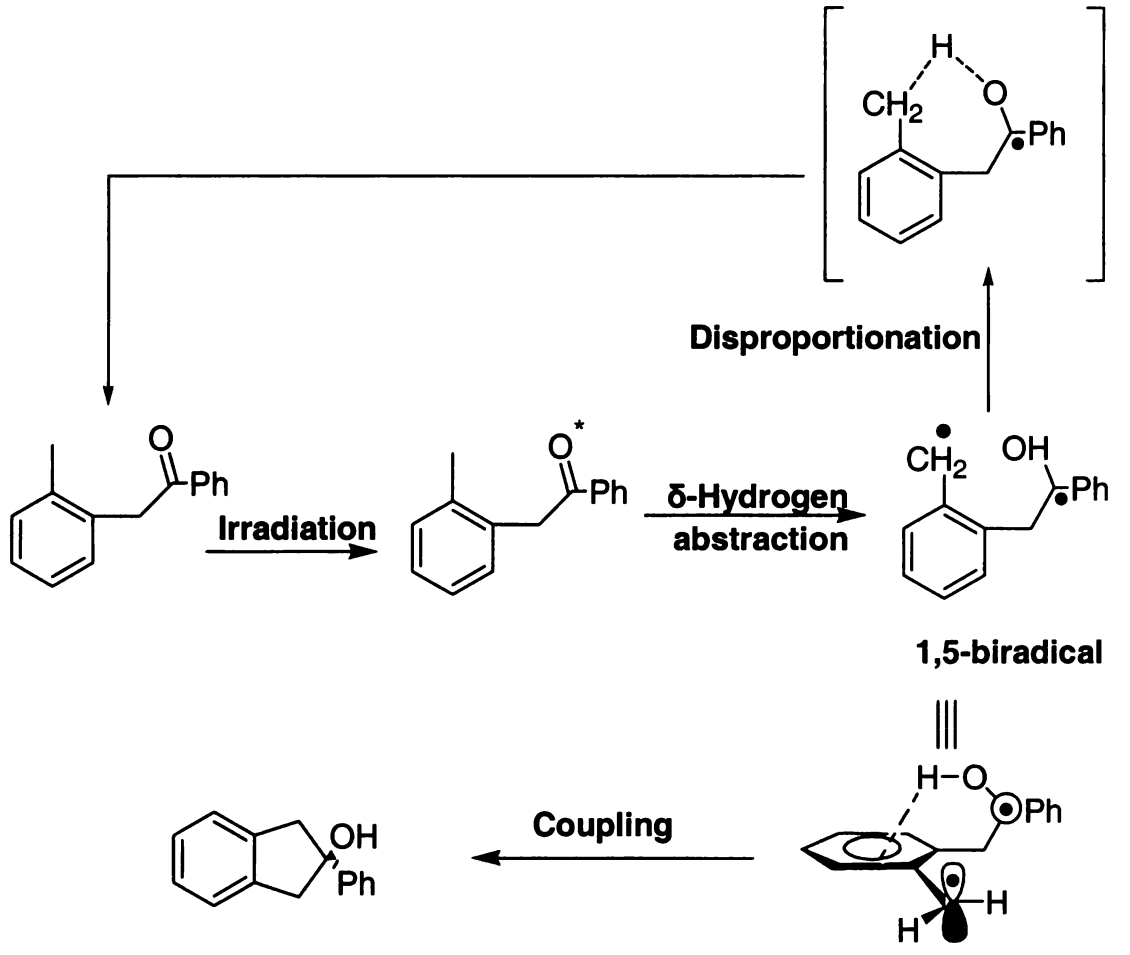
INTRODUCTION

I. Biradical Behavior during Photocyclization of α-Arylacetophenones

It has been reported by Wagner *et. al.* that α-(*o*-tolyl)acetophenone undergoes very efficient n,π* triplet state cyclization in benzene via δ-hydrogen atom abstraction to form 2-phenyl-2-indanol with quantum yield equal to unity. [1]

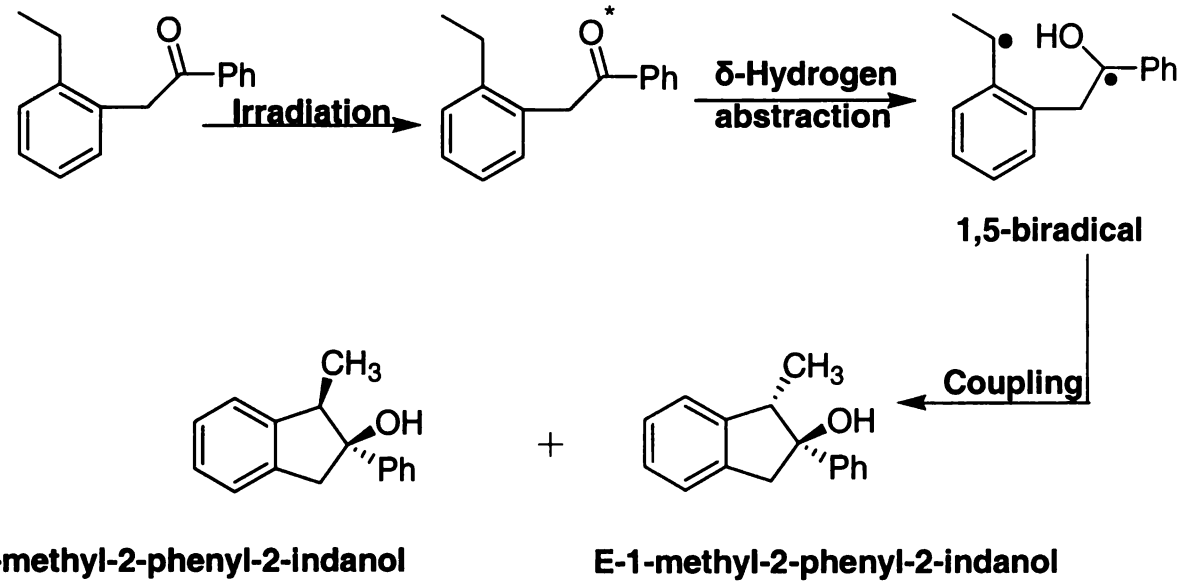


Scheme 1. Formation of 2-Phenyl-2-indanol from Irradiation of α-(*o*-Tolyl) acetophenone.

The 100% quantum yield indicates that the 1, 5-biradical intermediate undergoes no reactions that compete effectively with cyclization. The preferred

conformation of the 1, 5-biradical intermediate is stabilized by intramolecular OH-to-benzene ring hydrogen bonding [2] as shown in scheme 1, and this conformation can prevent reversion of the biradical intermediate to the ground state ketone via disproportionation. Thus high quantum efficiency of cyclization was observed.

α-(*o*-Ethylphenyl)acetophenone, however, undergoes photocyclization with quantum yield smaller than 100%,[3] which indicates that disproportionation back to the ground state ketone is now competing with cyclization process for the corresponding 1, 5-biradical intermediate.



Scheme 2. Formation of *Z*- and *E*-1-Methyl-2-phenyl-2-indanol from Irradiation of α-(*o*-Ethylphenyl)acetophenone.

Furthermore, the diastereoselectivity of the two cyclization products is solvent-dependent, as shown in table 1, with the one having its methyl and phenyl group *trans* to each other being favored.

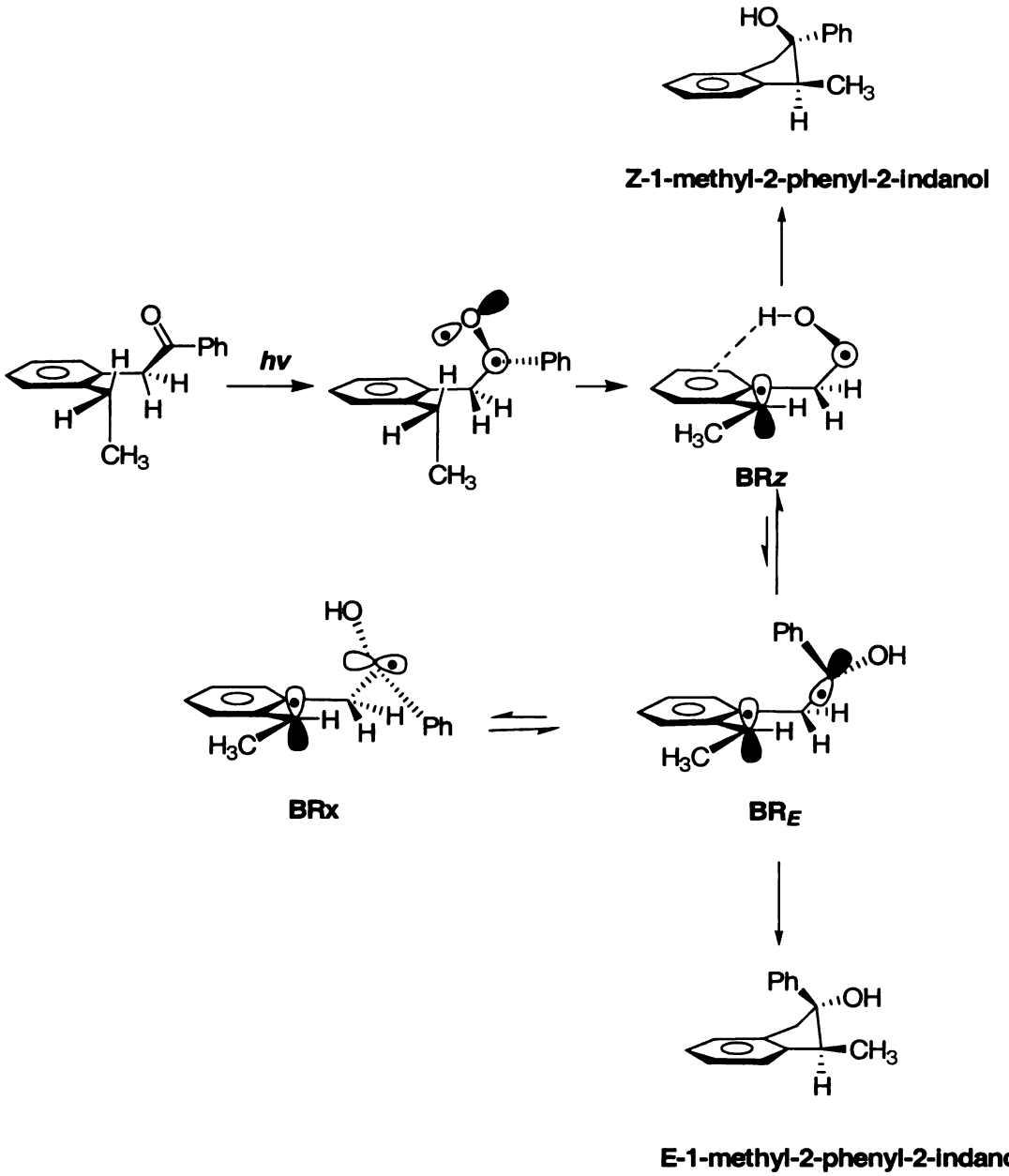
Table 1. Solvent effect on cyclization diastereoselectivity[a] of *α*-(*o*-Ethylphenyl)acetophenone [3, 4]

Solvent	Z-indanol/ E-indanol Ratio
Benzene	14.6:1 (0.48)[b]
Methanol	2:1

[a]Irradiation under room temperature.

[b] Product quantum yield in parentheses.

Analysis of the possible biradical conformations indicates that in the biradical intermediate, the stereochemistry is set prior to cyclization,[5] as shown in scheme 3:



Scheme 3. Biradical Conformations during Cyclization of α-(*o*-Ethylphenyl) acetophenone.

In the above scheme, BR*z*, BR_E and BRx are computed to be the three minimum energy geometries of the intermediate 1, 5-biradical. BR*z* and BR_E can undergo least motion cyclization to *Z* and *E* indanols, respectively, while BRx must rotate into one of the other two in order to cyclize.

Furthermore, BR*z* is calculated to be 1.6 kcal/mol more stable than BR_E. This can be understood by both steric and electronic point of views:

1) Sterically speaking, the phenyl group on one radical center prefers to be twisted away from the central benzene ring and the methyl group on the other radical center prefers to be twisted away from the large ortho substituent, so they tend to end up *trans* to each other when the two biradical ends rotate together.
2) Electronically speaking, the intramolecular O-H-to-benzene ring hydrogen bonding in the BR*z* conformation helps stabilize the BR*z* conformer. [6, 7] There is no such hydrogen bonding in BR_E conformer.

The first point was supported by the fact that diastereoselectivity decreases dramatically when solvent changing from benzene to methanol. Since in methanol, the OH group is solvated by hydrogen bonding, it is now comparable in size to the phenyl group such that the two rotamers (BR*z* and BR_E) are nearly equal in energy.

II. Goal of Research

The goal of this research work is to get experimental results to support the hypothesis that O-H-to-benzene ring hydrogen bonding in the biradical conformations formed during irradiation of α-arylacetophenones have stabilization effect for the conformers.

To achieve this goal, changes of the strength of the abovementioned intramolecular hydrogen bonding have been made by putting different ring substituents onto the *α*-aryl ring, both electron-withdrawing and electron-donating.

Diastereoselectivity of the photocyclization products have been measured for two substituted *α*-(*o*-Ethylphenyl) acetophenones. And the results have been compared to the product diastereoselectivity of their non-substituted analog to see the effect of hydrogen bonding on product diastereoselectivity.

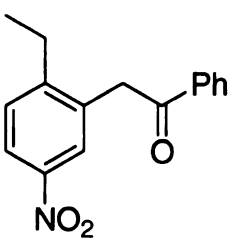
Since this kind of intramolecular hydrogen bonding can prevent reversion of the biradical intermediate to the ground state ketone via disproportionation, the quantum yield of photocyclization is also expected to be effected when the strength of this intramolecular hydrogen bonding changes. So quantum yields of cyclization have been measured for the abovementioned two substituted α-(*o*-ethylphenyl)acetophenones and the results have been compared with their non-substituted analog. At the same time, cyclization quantum yields of two substituted α-(*o*-tolyl) acetophenones have also been measured to see if the values change in the same trend as their α-(*o*-ethylphenyl) analogs.

Furthermore, different substituents on the α-aryl ring can also affect the rate of hydrogen abstraction.[5] So the rates have been calculated for those substituted α-(*o*-ethylphenyl)-and α-(*o*-tolyl)acetophenones by measuring triplet lifetimes of biradicals using quenching study.

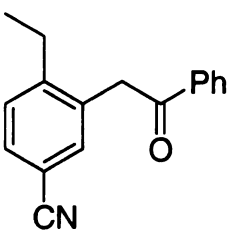
RESULTS

I. General Preparation of the Ketones

Substituted α-(*o*-Ethylphenyl)-acetophenones and α-(*o*-tolyl)acetophenones were similarly prepared from the corresponding substituted 2-bromo-1-ethylbezne and 2-bromotoluene by coupling with acetophenone using palladium (II) catalyst. [8,9] As a result, the following compounds were prepared and used in this study.



1



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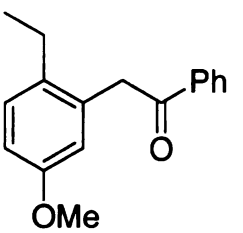

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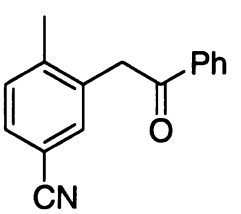

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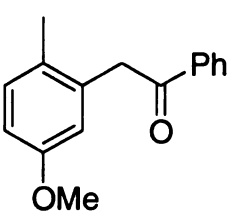

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II. Irradiation of ketones

NMR scale irradiations were carried out on 0.1M solutions of ketones in deuterated benzene. In order to achieve n, π^* excitation, the ketones were

irradiated through Pyrex (>290 nm) filter. A medium pressure mercury arc lamp served as the light source. For substituted α-(*o*-ethylphenyl)-acetophenones, **2** and **3,** they were irradiated at 0°C, room temperature (25 °C), 45 °C and 75 °C to determine the effect of temperature on product ratios. The desired temperatures were attained by ice-water, water (at room temperature) and heated silicon oil baths, respectively. For substituted α-(*o*-Tolyl)-acetophenones, they were only irradiated at room temperature(25 °C). In most cases, the starting ketones disappeared within 24 hours' irradiation with the apprearance of corresponding 2-phenyl-2-indanols as the photoproducts and material balance were > 95%. Ketone **1** is an exception, after irradiation for 20 days at room temperature, no change in ^{1}HNMR was observed.

Chemical yields were measured by irradiating 0.02M solutions of ketones in purified benzene at room temperature (25°C). Silica gel column chromatography was used to separate and purify the photoproducts.

For substituted α-(*o*-Ethylphenyl)-acetophenones **2** and **3**, the structure assignments of the diastereomeric photoproducts were straightforward. Methyl doublet at 0.6-1.5ppm were most informative since it is generally accepted that a methyl cis to the phenyl is significantly shielded relative to one trans, as previously observed in a number of such products. [10, 11, 12] For example, in photoproducts from α-(*o*-Ethylphenyl)-acetophenone, the chemical shifts of methyl group of E isomer was shifted much more upfield than that of Z isomer, as shown in scheme 4 .

E-isomer Z-isomer

Scheme 4. Chemical Shifts (in $CDCl_3$)of Methyls Trans and Cis to Phenyl in Five-Membered Rings.

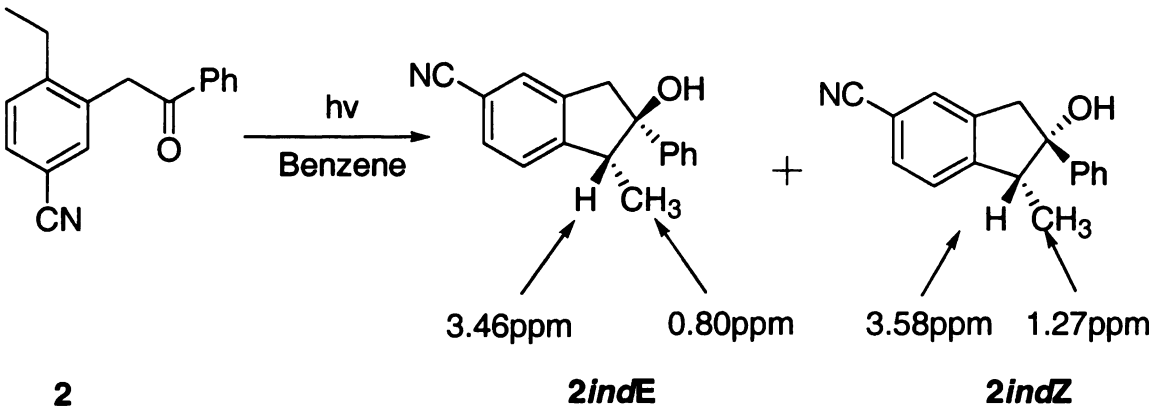
1. α-(2-Ethyl-5-nitrophenyl)acetophenone (1)

After 20 days' irradiation at room temperature in benzene, no significant change in ^1H NMR compared with the ketone reactant was observed.

2. α-(5-Cyano-2-ethylphenyl)acetophenone (2)

Under various irradiation temperatures, the starting ketone disappeared after 15-24 hours' irradiation with the corresponding appearance of diastereomeric mixtures of 2-phenyl-2-indanols. Quantitative analysis of chemical yields and photoproduct ratios were achieved by NMR analysis of the resulting mixtures.

Preparative scale irradiation of **2** followed by column chromatography on silica resulted in separation of the two products which were identified as two isomeric 2-phenyl-2-indanols (***2indZ*** and ***2indE***) by their NMR spectra in CDCl3 (Scheme 5).



Scheme 5. Photochemistry of α-(5-Cyano-2-ethylphenyl)acetophenone.

NOE experiments also confirmed this assignment. For the photoproduct having methyl doublet at 0.80ppm, this doublet was irradiated and enhancement resonance of aromatic protons was observed. It indicates that the methyl and phenyl ring are cis to each other in this product. The methyl doublet at 1.27ppm for the other photoproduct was also irradiated and no such enhancement was observed. Instead, irradiation of the methine quartet at 3.58ppm leaded to enhancement resonance of aromatic protons, which indicates the hydrogen in methine and the phenyl ring are cis to each other.

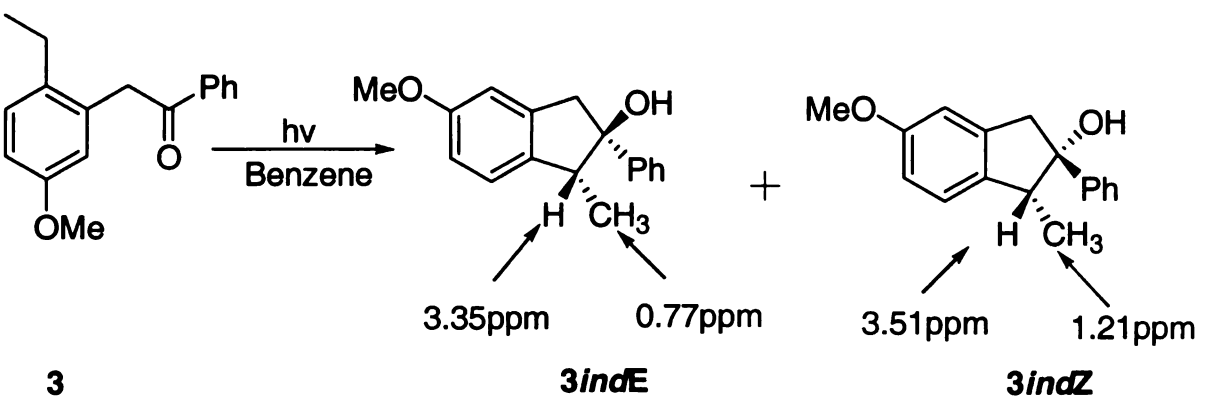
Quantitative analysis of product ratio at several temperatures was achieved by irradiating 0.1M solution of **2** in benzene-d6 through a Pyrex filter followed by NMR analysis. Table 2 shows the result of temperature effect study for ketone **2.**

Table 2. Chemical yields and ratios of photoproducts from ketone 2 in benzene-d_6 at various temperatures (λ>290 nm)

Temperature(°C)	%2*indE*	%2*indZ*	Z/E ratio
0	9.9	89.3	9.0
25	10.4	89.2	8.6
45	11.9	87.6	7.4
75	14.1	85.6	6.1

3. α-(2-Ethyl-5-methoxyphenyl)acetophenone (3)

Irradiation of a 0.1 M solution of **3** in benzene-d_6 resulted in formation of two isomeric 2-phenyl-2-indanols (**3*indZ*** and **3*indE***, Scheme 6). Preparative scale irradiation of **2** in benzene followed by column chromatography on silica resulted in separation of the two products, which were identified from their corresponding NMR spectra in $CDCl_3$, each isomer showing a methyl doublet, a methine quartet and an AB quartet signal with coupling constants similar to previously identified indanols.[3, 13, 14] The NMR signal of the cis methyl appears at 1.21ppm while that of the trans methyl appears at 0.77ppm.



Scheme 6. Photochemistry of α-(2-Ethyl-5-methoxyphenyl)acetophenone.

NOE experiments also confirmed this assignment. For the photoproduct having methyl doublet at 0.77ppm, this doublet was irradiated and enhancement resonance of aromatic protons was observed. It indicates that the methyl and phenyl ring are cis to each other in this product. The methyl doublet at 1.21ppm for the other photoproduct was also irradiated and no such enhancement was observed. Instead, irradiation of the methine quartet at 3.51ppm led to enhancement resonance of aromatic protons, which indicates the hydrogen in methine and the phenyl ring are cis to each other.

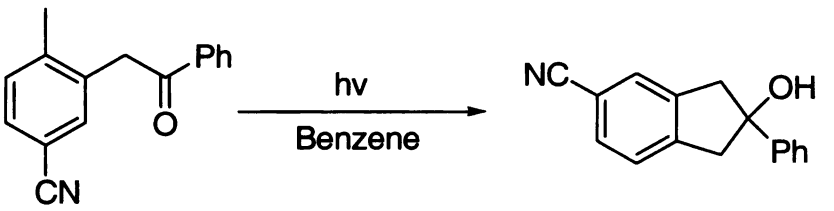
The product ratios were determined by intergration of the methyl doublet signals of each isomer. Chemical yields and product ratios under several reaction temperatures are listed in Table 3.

Table 3. Chemical yields and ratios of photoproducts from ketone 3 in benzene-d_6 at various temperatures (λ>290 nm)

Temperature(°C)	%3*ind*E	%3*ind*Z	Z/E ratio
0	4.6	94.4	20.5
25	5.1	94.0	18.3
45	5.9	93.7	16.0
75	6.0	93.4	15.7

4. *α*-(5-Cyano-2-methylphenyl)acetophenone (4)

Irradiation of 0.1M solution of **4** in benzene-d_6 at room temperature results in formation of 5-cyano-2-phenyl-indan-2-ol (***4ind,*** Scheme 7) as the only photoproduct in a quantitative way.

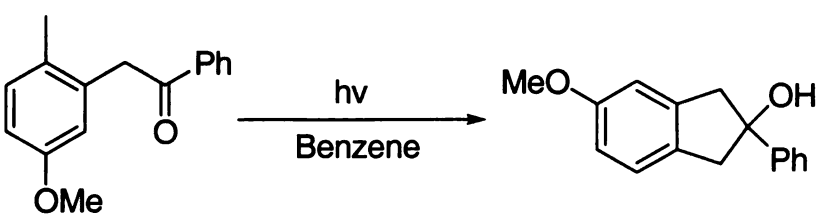


4 ***4ind***

Scheme 7. Photochemistry of α-(5-Cyano-2-methylphenyl)acetophenone.

5. *α*-(5-Methoxy-2-methylphenyl)acetophenone (5)

Irradiation of 0.1M solution of **5** in benzene-d_6 at room temperature results in formation of 5-methoxy-2-phenyl-indan-2-ol (***5ind,*** Scheme 8) as the only photoproduct in a quantitative way.



5 ***5ind***

Scheme 8. Photochemistry of α-(5-Methoxy-2-methylphenyl)acetophenone.

III. Steady-State Photokinetics.

The quantum yields were measured by irradiation of degassed solutions of ketones in tubes containing a fixed amount of internal standard parallel to valerophenone actinometer [15] at 313nm. For quenching studies, these tubes also contained varying amounts of 2,5-dimethyl-2,4-hexadiene quencher. [16] Product yields around 10% to 20% were measured using GC analysis and were converted to quantum yields. Stern-Volmer plots [17] were linear with slopes equal to $K_q\tau$. The kinetic data are listed in table 4 and 5. Triplet lifetimes, based on a K_q value of $6\times10^9 M^{-1}S^{-1}$,[18] are also listed. The errors represent deviation of 2-4 measured values from the average.

Table 4. Lifetimes of Triplet Acetophenones in Benzene

Ketones	$K_q\tau$, M^{-1}	$1/\tau$, 10^9 S^{-1}
2	14.49 ± 0.6	0.41
3	2.54 ± 0.1	2.36
4	53.12 ± 0.5	0.11
5	14.89 ± 0.4	0.40

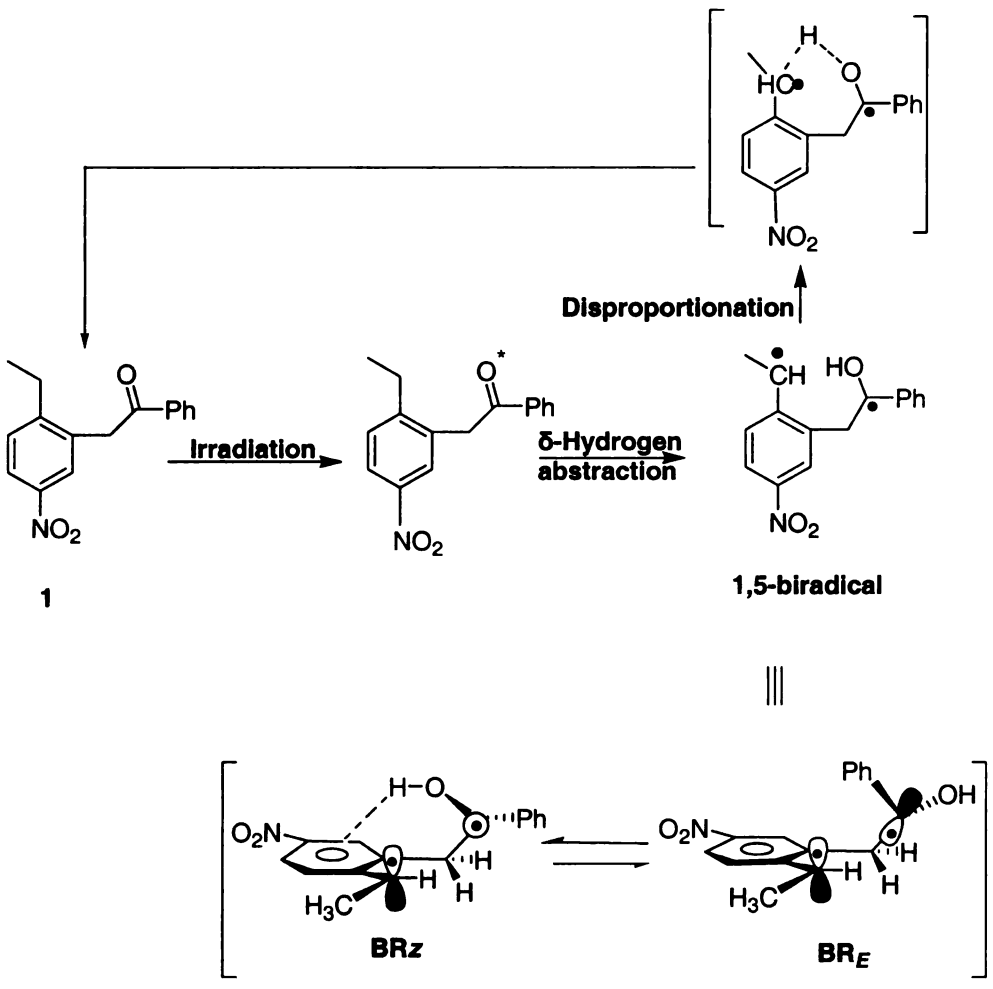
Table 5. Quantum Yields of Photoproducts from Acetophenones in Benzene (measured at 313nm)

Ketones	$\Phi_{cyc.}$
2	0.292±0.013
3	0.601±0.013
4	0.342±0.002
5	0.978±0.012

DISCUSSION

I. The Reason for Non-reactivity of α-(2-Ethyl-5-nitrophenyl)acetophenone (1) toward Irradiation

UV experiments showed that for 4-ethyl-nitrobenzene, ε_{313nm}=132.8, while for ketone **1**, ε_{313nm}=241.5 and for *α*-(*o*-Ethylphenyl)acetophenone, ε_{313nm}=116.9. The ratio of the values between 4-ethyl-nitrobenzene and ketone **1** is about 55: 100. It indicates that for ketone **1**, among every 100 protons it absorbs, there are 55 photons being absorbed by the NO_2 chromophore, instead of being absorbed by the carbonyl group. Furthermore, the strong electron-withdrawing effect of the nitro substituent on *o*-ethylphenyl ring decreases the nucleophilicity of the benzene ring thus weaken the OH-to-benzene ring hydrogen bonding in BRz conformation. The biradical is now easier to reverse back to ground state ketone via disproportination than when there is strong intramolecular hydrogen bonding in BRz conformation. These reasons explain partially why photolysis of ketone **1** proceeded at such a slow rate.



Scheme 9. Disproportionation of 1,5 biradical to the Ground State Ketone during Irradiation of α-(2-Ethyl-5-nitrophenyl)acetophenone.

II. Substituent and Temperature Effect on Product Diastereoselectivity in Photocyclization of α-(5-Cyano-2-ethylphenyl)acetophenone (2) and α-(2-Ethyl-5-methoxyphenyl)acetophenone(3)

1. Substituent Effect on Product Diastereoselectivity in Photocyclization of some α-(o-Ethylphenyl)acetophenones

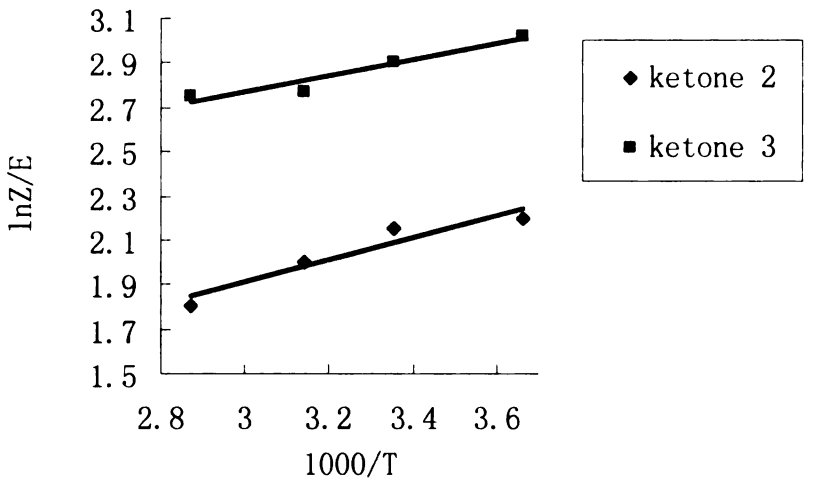
Ali R. Zand studied for the product diastereoselectivity of α-(o-ethylphenyl)acetophenone. [3] The ratio of Z/E-indanol equals to 14.6 at room temperature. Having an electron-withdrawing group substituted on the ethylphenyl ring, α-(5-Cyano-2-ethylphenyl)acetophenone (**2**) gives a lower product ratio of 8.6 under same reaction temperature. On the other hand, for α-(2-Ethyl-5-methoxyphenyl)acetophenone(**3**), this ratio increases to 18.3.

These experimental results support the hypothesis mentioned in the introduction part that intramolecular O-H-to-benzene ring hydrogen bonding can stabilize the BR*z* conformation shown in scheme III. Since electron donating substituents like methoxy group will increase the nucleophilicity of the benzene ring and thus enhance the strength of the O-H-to-benzene ring hydrogen bonding, BR*z* is more favored over BR_E than in the case when there is no substituent on the benzene ring. So the stereoselectivity of cyclization was enhanced. On the other hand, an electron withdrawing substituent such as a cyanide group will have exactly the opposite effect resulting in weaker O-H-to-benzene ring hydrogen bonding and lower product stereoselectivity.

2. Temperature effect on product Diastereoselectivity

For ketone **2** and **3**, the same trend of temperature effect was observed on photoproduct diastereoselectivity. That is, the selectivity decreases when temperature goes up. The same trend was also observed for non-substituted

ketone, α-(o-ethylphenyl)acetophenone, which was studied by Dr. Zand. [3] These results indicate that not only the activation enthalpy difference in BR*z* and BR_E, but also the entropies may be responsible for the observed diasteroselectivity. Since BR_E conformer is the one with higher rotational freedom, it might be more favored at higher temperature than when the reaction is running under lower temperature.



Graph 1. Arrhenius plot of temperature effect for ketones 2 and 3.

Graph 1 shows the Arrhenius plot of ketones **2** and **3** under various irradiation temperature. According to the Arrhenius equation, $K= Ae^{-Ea/RT}$, the following Arrhenius data can be obtained in table 6.

Table 6. Arrhenius Data from Graph 1.

Ketone	A_z/A_E	ΔEa, Kcal/mole
2	$A_z/A_E=1.5$	$E_E-E_Z=1.02$
3	$A_z/A_E=5.4$	$E_E-E_Z=0.73$

III. Substituent Effect on Steady-state Photokinetics of α-(o-Ethylphenyl) acetophenones and α-(o –Tolyl)acetophenones

When comparing cyclization quantum yields of three α-(o-Ethylphenyl) acetophenones as shown in Table 6, an obvious trend can be observed. Ketone **2**, with an electron-withdrawing cyanide group substituted on the ethylphenyl ring, has a lower cyclization quantum yield than its non-substituted analog, while ketone 3 with an electron-donating methoxy group substituted on the same position has a higher value. A similar trend can be found by comparing cyclization quantum yields of three α-(o –Tolyl)acetophenones which are also listed in table 6.

These results again support the hypothesis mentioned in the introduction part that intramolecular O-H-to-benzene ring hydrogen bonding can stabilize the BR*z* conformation shown in scheme 3. The electron-withdrawing cyanide group in ketones **2** and **4** decreases nucleophilicity of the benzene ring and results in weaker Hydrogen bonding. An electron donating methoxy group in ketones **3** and **5**, on the other hand, strengthen the hydrogen bonding by donating electron density into the benzene ring. Since such kind of intramolecular hydrogen bonding can prevent reversion of the biradical intermediate back to the ground state ketone via disproportionation, a stronger hydrogen-bonding results in a higher Cyclization quantum yield.

Since the reactive n, π* triplet is a very electron-deficient species, electron-withdrawing substituents near the C-H bond being attacked strongly decrease the rate constant and electron-donating substituents increase rate constant. [5]

That's exactly what can be seen from the results in table 6. ketones **2** and **4** with electron-withdrawing cyanide substituted have slower hydrogen abstraction rate than their non-substituted analog, while ketones **3** and **5** abstract hydrogen faster than their non-substituted analog.

Table 7. Cyclization quantum yield and rate of hydrogen abstraction of non-substituted and some substituted α-(o-Ethylphenyl)- acetophenones and α-(o –Tolyl)acetophenones

Ketones	$\Phi_{cyc.}$	$1/\tau$, 10^9 S^{-1}
α-(o-Ethylphenyl)acetophenone [3]	0.48	1.08
2	0.29	0.41
3	0.60	2.36
α-(o –Tolyl)acetophenone [1]	1.00	0.16
4	0.34	0.11
5	0.98	0.40

EXPERIMENTAL

I. General Procedures

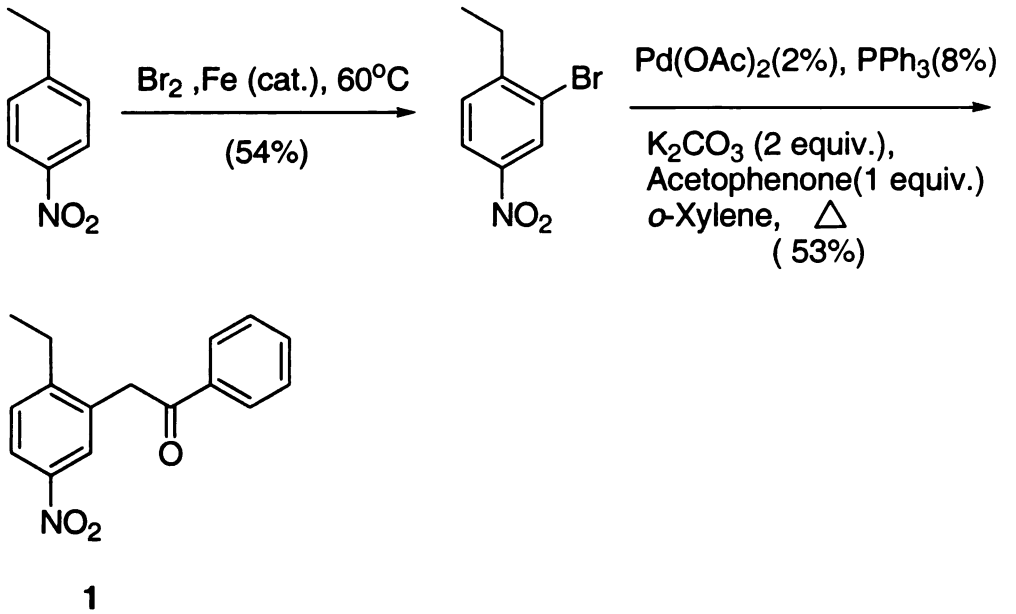
^{1}H NMR and ^{13}C NMR spectra were recorded primarily on Varian Unity+-500 and Varian Gemini-300 NMR spectrometers in $CDCl_3$ except where noted. IR spectrum on a Nicolet IR/42 spectrometer, UV spectra on either a Shimadza UV-160 or a Hewlett Packard 8453 spectrometer, GC analyses on either a Varian 1400 or a Hewlett Packard 5890 Series II Gas Chromatography.

II. Preparation of Starting Ketones

All new compounds were analyzed by CHN elemental analysis on a Perkin Elmer Series II CHN S/O Analyser 2400 instrument or by high resolution mass spectra on a Joel JMS-HX110 Mass spectrometer in the MSU Mass Spectroscopic facility.

α-(2-Ethyl-5-nitrophenyl)acetophenone (1)

4-nitroethylbezene (Alfa Aesar) was brominated with bromine catalyzed by iron powder. [19] The resulting bromide was coupled with acetophenone using palladium (II) catalysis to form ketone **1**. [20]



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Scheme 10. Preparation of *α*-(2-Ethyl-5-nitrophenyl)acetophenone.

2-bromo-4-nitroethylbezene

To a 100mL three-necked round bottom flask equipped with a thermometer, a condenser, a magnetic stir bar and purged with nitrogen gas, 20.0 grams (0.132 moles) of 4-nitroethylbenzene and 0.6 grams (0.0107mol) of iron (reduced by hydrogen) was added. The flask was wrapped with aluminum foil and the reaction was allowed to run in the dark to avoid radical reactions. When temperature increased to 40^{0}C, 21.6 grams (0.135 moles) of bromine was added from syringe drop by drop to the flask with stirring. The mixture was allowed to stir at 60°C for 60 hours. Then the reaction mixture was extracted by ether three times. The combined ether layer was washed by brine and dried over anhydrous sodium sulfate. Solvent was then removed to afford 27.02g brown oil. Analysis of the oil showed it to contain the desired product, the starting material and some poly-brominated byproducts. Fractional distillation resulted in recovery of 7.8g

starting material and 10.0g of desired product (54% yield, based on recovery) as yellow oil.

^{1}H NMR ($CDCl_3$): δ1.24(t, *J* = 7.5 Hz, 3 H), 2.83(q, *J* = 7.5 Hz, 2 H), 7.38(d, *J* = 4.5 Hz, 1 H), 8.09(d, *J* = 8.4 Hz, 1 H), 8.38(s, 1 H).

α-(2-Ethyl-5-nitrophenyl)acetophenone

To a 100mL three-necked round bottom flask equipped with a thermometer, a condenser, a magnetic stir bar and purged with nitrogen gas, 0.090 grams (0.0004 moles) of palladium (II) acetate, 0.42 grams (0.0016 moles) of triphenylphosphine and 5.53 grams (0.04 moles) of potassium carbonate was added. Then 50mL of o-xylene was added by syringe. With stirring, 4.6 grams (0.02 moles) of 2-bromo-4-nitroethylbezene dissolved in 5 mL of o-xylene was added by syringe, followed by 2.4 grams (0.02 moles) of acetophenone. The mixture was refluxed for 96 hours. Then the reaction mixture was extracted by ether three times. The combined ether layer was washed by brine and dried over anhydrous sodium sulfate. Solvent was then removed to afford a mixture of yellow oil. Analysis of the oil showed it to contain the desired product and the starting materials. After silica gel chromatography (using 15:1 hexane/ethyl acetate solution as eluent), 2.22 grams of the desired ketone was obtained (53% yield, based on recovery) together with 1.02 grams of the starting bromide.

^{1}H NMR($CDCl_3$): δ1.21(t, *J* = 7.5 Hz, 3 H), 2.63 (q, *J* = 7.5 Hz, 2 H), 4.43(s, 2 H), 7.39 (d, *J* = 8.5 Hz, 1 H), 7.51 (t, *J* = 7.5 Hz, 2 H), 7.62 (t, *J* = 7.5 Hz, 1 H), 8.00-8.04 (m, 3 H), 8.10 (dd, *J* = 8.5, 2 Hz, 1 H)

^{13}C NMR($CDCl_3$): δ14.5, 26.4, 42.8, 122.8, 126.1, 128.5, 129.2, 129.4, 134.0, 134.6, 136.6, 146.4, 150.9, 196.3

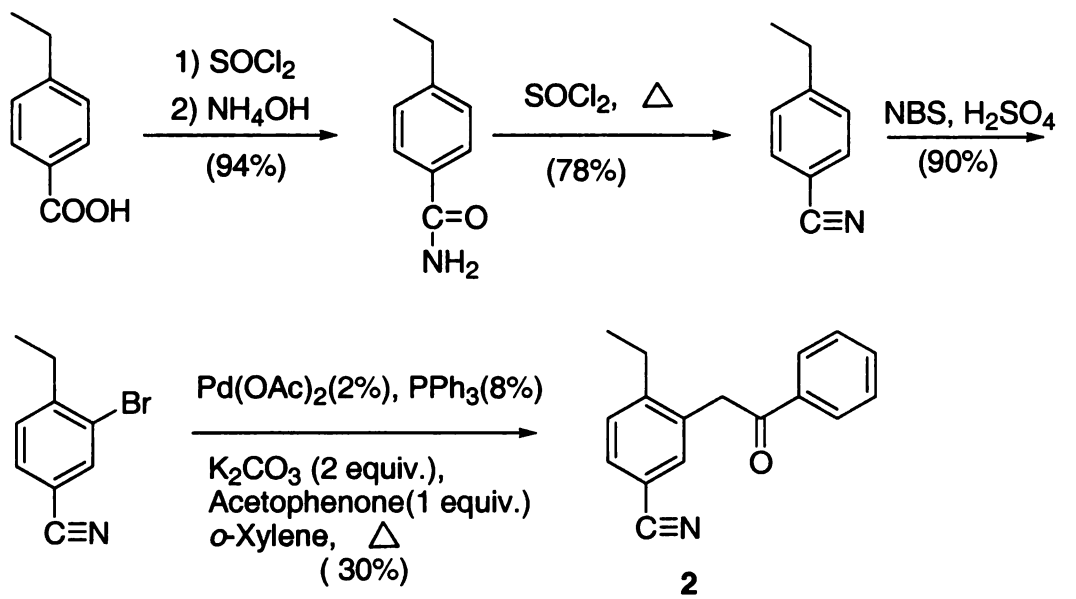
IR (CCl_4): 1688, 1518, 1348, 1211cm^{-1}

m.p.: 83.3-84.7 °C

HRMS (FAB): m/z 270.1129 (MH^+).

α-(5-Cyano-2-ethylphenyl)acetophenone (2)

4-Ethylbenzioc acid (Aldrich) was first transformed to the corresponding acyl chloride with thionyl chloride. 4-Ethylbenzamide was then obtained by reacting the acyl chloride with aqueous ammonia (3M).[21] Dehydration of this amide furnished 4-ethylbenzonitrile.[22] Bromination of the nitrile [23] followed by coupling with acetophenone using palladium (II) catalysis [20] gave ketone **2.**



Scheme 11. Preparation of α-(5-Cyano-2-ethylphenyl)acetophenone.

4-Ethylbenzamide

To a 100 mL round bottom flask equipped with a condenser, a magnetic stir bar and purged with nitrogen gas, 10 grams of 4-ethylbenzioc acid was added. The flask was then heated in a water bath. When the temperature of the water bath reached 50^0C, 9 mL of thionyl chloride and 20 drops of dimethylfomamide were added dropwise with stirring. Then the mixture was stirred for 15 minutes at 50-60^0C until all acid was dissolved. The mixture was then added drop by drop into 200 mL ice-cold ammonium hydroxide (3M) with stirring. Suction filtration of the mixture afforded 9.37 grams (94% yield) of product as white solid. This solid was used without further purification in the next step.

^{1}H NMR ($CDCl_3$): δ 1.13 (t, J = 7.5 Hz, 3 H), 2.58 (q, J = 7.5 Hz, 2 H), 5.90-6.10 (bs, 2 H), 7.15 (d, J = 8.4 Hz , 2 H), 7.62 (d, J = 8.1Hz, 2 H)

4-ethylbenzonitrile

To a 50 mL round bottom flask equipped with a condenser, a magnetic stir bar and purged with nitrogen gas, 9.37 grams (0.063 moles) of 4-Ethylbenzamide and 7 mL (0.096 moles) of thionyl chloride were added. The mixture was refluxed for 1 hour. The excess thionyl chloride was removed by rotatory evaporator. Vacuum distillation afforded 6.7g crude product (b.p. = 64-67°C/3mmHg). After silica gel chromatography (using 80:1 hexane/ethyl acetate solution as eluent), 6.54 grams (78% yield) of pure product was obtained.

^{1}H NMR ($CDCl_3$): δ 1.22 (t, J = 7.5 Hz, 3 H), 2.68 (q, J = 7.5 Hz, 2 H), 7.26 (d, J = 7.8 Hz , 2 H), 7.53 (d, J = 8.1 Hz , 2 H)

3-bromo-4-ethylbenzonitrile

To a 100 mL round bottom flask equipped with a magnetic stir bar, 6.54 grams (0.050 moles) of 4-ethylbenzonitrile and 30 mL of sulfuric acid aqueous solution (concentrated sulfuric acid :water = 1:1,v/v) were added. The flask was wrapped with aluminum foil and the reaction was allowed to run in the dark to avoid radical reaction. After the mixture was stirred for 10 minutes, 8.9 grams (0.050 moles) of N-bromo-succinimide was added to the flask slowly over 20 minutes. The mixture was stirred at room temperature for 2 days. Then the reaction mixture was extracted by ether three times. The combined ether layer was washed with brine and dried over anhydrous sodium sulfate. Solvent was removed to afford crude product as a pale-yellow solid. After silica gel chromatography (using 80:1 hexane/ethyl acetate solution as eluent), 9.43 grams (90% yield) of pure product was obtained.

^{1}H NMR ($CDCl_3$): δ 1.22 (t, *J* = 7.5 Hz, 3 H), 2.79 (q, *J* = 7.5 Hz, 2 H), 7.31 (d, *J* = 7.8 Hz , 1 H) 7.52 (d, *J* = 7.2 Hz , 1 H), 7.80 (s, 1 H)

α-(5-Cyano-2-ethylphenyl)acetophenone

To a 250 mL three-necked round bottom flask equipped with a thermometer, a condenser, a magnetic stir bar and purged with nitrogen gas, 0.198 grams (0.00088 moles) of palladium (II) acetate, 0.923 grams (0.00352 moles) of triphenylphosphine and 12.2 grams (0.088 moles) of potassium carbonate was added. Then 80 mL of o-xylene was added by syringe. With stirring, 9.24 grams

(0.044 moles) of 3-bromo-4-ethylbenzonitrile dissolved in 10 mL of o-xylene was added by syringe, followed by 5.29 grams (0.044 moles) of acetophenone. The mixture was refluxed for 3 days. Then the reaction mixture was extracted by ether three times. The combined ether layer was washed with brine and dried over anhydrous sodium sulfate. Solvent was then removed to afford a mixture of compounds as a yellow oil. Analysis of the oil showed it to contain the desired product and the starting materials. After silica gel chromatography (using 40:1 hexane/ethyl acetate solution as eluent), 1.77 grams of the desired ketone was obtained (30% yield, based on recovery) together with 4.26 grams of the starting bromide.

^{1}H NMR($CDCl_3$): δ 1.19 (t, J = 7.5 Hz, 3 H) 2.60 (q, J = 7.5 Hz, 2 H), 4.37 (s, 2 H), 7.33 (d, J = 8.1 Hz, 1 H), 7.40 (d, J = 1.5 Hz, 1 H), 7.48-7.54 (m, 3 H), 7.59 (t, J = 2 Hz, 1H), 7.99-8.02 (m, 2 H)

^{13}C NMR($CDCl_3$): δ 13.9, 25.8, 42.0, 109.6, 118.8, 128.0, 128.6, 128.8, 130.8, 133.4, 133.9, 135.9, 148.2, 196.0

IR (CCl_4): 2228, 1690 cm^{-1}

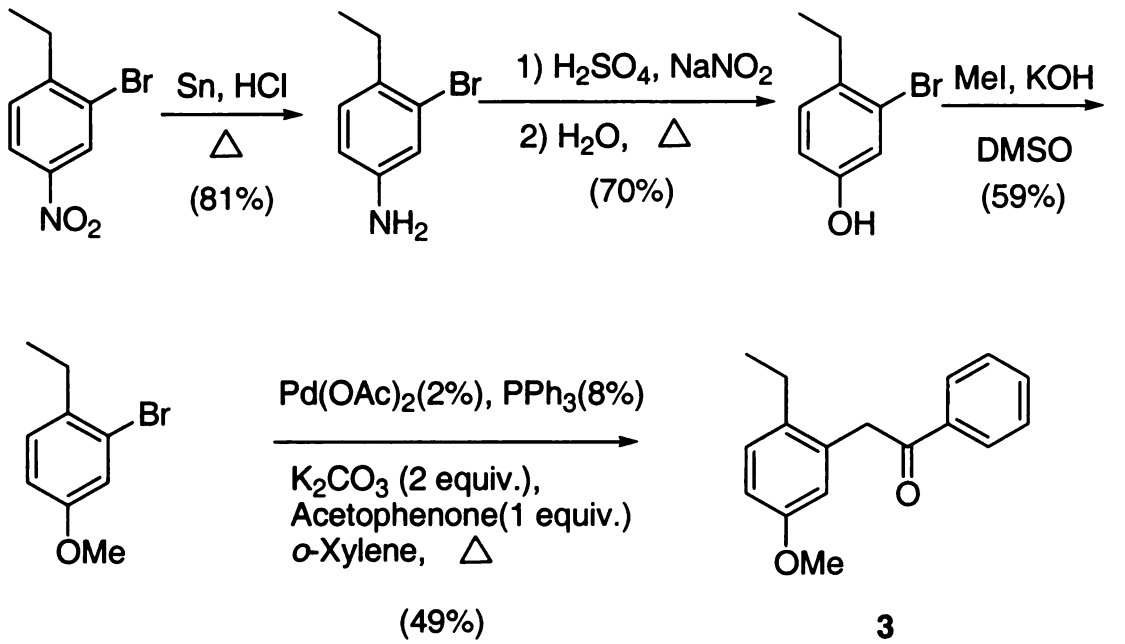
m.p.: 92.9-93.5 °C

HRMS (FAB): m/z 250.1233 (MH^+)

α-(2-Ethyl-5-methoxyphenyl)acetophenone (3)

Reduction of 2-bromo-4-nitroethylbenzene formed the corresponding aniline,[24] which was then subjected to a Sandmeyer reaction to obtain 3-bromo-4-ethyl-phenol.[25] Methylation of the phenol with potassium hydroxide and methyl iodide

afforded 3-bromo-4-ethyl-anisole [26] which was coupled with acetophenone using palladium (II) catalysis [20] to furnish ketone **3**.



Scheme 12. Preparation of α-(2-Ethyl-5-methoxyphenyl)acetophenone.

3-bromo-4-ethyl-aniline

To a 100 mL three-necked round bottom flask equipped with a thermometer, a condenser, a magnetic stir bar and purged with nitrogen gas, 6.50 grams (0.055 moles) of finely divided tin powder and 5.65 grams (0.0246 moles) of 2-bromo-4-nitroethylbenzene was added. The flask was cooled by an ice-water bath while 20 mL of concentrated hydrochloric acid was added dropwise with stirring. The rate of acid addition was controlled so that the temperature was maintained below 60 °C. After the initial exothermic portion of the reaction was complete, the ice water bath was removed and the reaction mixture was refluxed for 40 minutes.

After the mixture cooled down to room temperature, 10 M aqueous NaOH solution was added to make it basic. The organic layer was extracted by ether three times. The combined ether layer was washed with brine and dried over anhydrous sodium sulfate. Solvent was then removed to afford 4.08 grams (81% yield) of the product as a yellow oil.

^{1}H NMR($CDCl_3$): δ 1.16, (t, *J* = 7.5 Hz, 3 H,), 2.63 (q, *J* = 7.5 Hz, 2 H), 3.48-3.62 (bs, 2 H), 6.58 (dd, *J* = 8.4, 2.4 Hz, 1 H), 6.87 (d, *J* = 2.4 Hz, 1 H), 6.98 (d, *J* = 8.1 Hz 1 H)

3-bromo-4-ethyl-phenol

To a 250 mL three-necked round bottom flask equipped with a thermometer, a magnetic stir bar and purged with nitrogen gas, 4.97 grams (0.025 moles) of 3-bromo-4-ethyl-aniline was added. To it was added the hot diluted acid obtained by adding 4.5 mL of concentrated sulfuric acid into 12.5 mL of water. The clear solution was stirred and cooled to 15°C. Then 10 grams of ice was added. As soon as the temperature had dropped below 5°C, a solution of 2.01 grams (0.029 moles) of sodium nitrite in 6 mL of water was added from a syringe, the needle of which extended below the surface of the liquid. The temperature of the solution was kept below 5°C during addition. The solution was stirred for 5 minutes after addition. Then 5 mL of cold water, 0.19 grams of urea and 10 grams of cracked ice were added successively. The solution was kept in an ice water bath until used. To another 250 mL three-necked round bottom flask equipped with a condenser, a magnetic stir bar and purged with nitrogen gas, 9.4 grams of anhydrous sodium sulfate, 12.5 mL of concentrated sulfuric acid and 6 mL of

water were added. The mixture was boiled, them the solution of diazonium salt was added in portions. The mixture was refluxed for 1 hour. After it was cooled down to room temperature, the reaction mixture was extracted with two100 mL portions of ether, and the combined extracts were washed successively with 100 mL of water and 100 mL of 10% sodium bicarbonate solution. The phenol was then extracted from the ether layer by use of one 100 mL and two 50 mL portions of 10% NaOH solution. The combined alkaline solutions were acidified, with cooling, by the addition of 100 mL of concentrated hydrochloric acid. The phenol was then extracted with one 100 mL and two 50 mL portions of ether. The combined ether layer was washed with brine and dried over anhydrous sodium sulfate. Solvent was then removed to afford crude product as a brown oil. After silica gel chromatography (using 6:1 hexane/ethyl acetate solution as eluent), 3.45 grams (70% yield) of the product was obtained.

^{1}H NMR($CDCl_3$): δ 1.17, (t, J = 7.5 Hz, 3 H), 2.66 (q, J = 7.5 Hz, 2 H), 5.4-6.0 (bs, 1H), 6.73 (dd, J = 8.1, 2.4 Hz, 1 H), 7.04-7.07 (m, 2 H)

3-bromo-4-ethylanisole

To a 100 mL round bottom flask equipped with a magnetic stir bar and purged with nitrogen gas, 3.92 grams (0.07 moles) of powdered potassium hydroxide and 50 mL of dimethyl sulfoxide were added. After stirring for 5 minutes, 3.45 grams (0.017 moles) of 3-bromo-4-ethyl-phenol was added, followed immediately by 4.97 grams (0.035 moles) of methyl iodide. Stirring was continued for 3 hours. Then the mixture was poured into 200 mL of water and extracted three times with

100 mL portions of dichloromethane. The combined organic extracts were washed with brine and dried over anhydrous sodium sulfate. Solvent was then removed to afford crude product as a brownish red oil. After silica gel chromatography (using 80:1 hexane/ethyl acetate solution as eluent), 2.17 grams (59% yield) of the product was obtained.

^{1}H NMR($CDCl_3$): δ 1.18 (t, J = 7.5 Hz, 3 H,), 2.68 (q, J = 7.5 Hz, 2 H), 3.76 (s, 3 H), 6.79 (dd, J = 8.6, 2.7 Hz, 1 H), 7.08 (d, J = 2.7 Hz, 1 H), 7.11 (d, J = 8.4 Hz, 1 H)

α-(2-Ethyl-5-methoxyphenyl)acetophenone

To a 100 mL three-necked round bottom flask equipped with a thermometer, a condenser, a magnetic stir bar and purged with nitrogen gas, 0.045 grams (0.0002 moles) of palladium (II) acetate, 0.210 grams (0.0008 moles) of triphenylphosphine and 2.76 grams (0.02 moles) of potassium carbonate was added. Then 40 mL of o-xylene was added by syringe. With stirring, 2.17 grams (0.01 moles) of 3-bromo-4-ethylanisole dissolved in 5 mL of o-xylene was added by syringe, followed by 1.20 grams (0.01 moles) of acetophenone. The mixture was refluxed for 24 hours. Then the reaction mixture was extracted with ether three times. The combined ether layer was washed with brine and dried over anhydrous sodium sulfate. Solvent was then removed to afford a yellow solid. Analysis of the solid showed it to contain the desired product and the starting materials. After silica gel chromatography (using 40:1 hexane/ethyl acetate solution as eluent), 1.25 grams of the product was obtained (49% yield).

^{1}H NMR($CDCl_3$): δ 1.16 (t, J = 7.5 Hz, 3 H,), 2.53 (q, J = 7.5 Hz, 2 H), 3.74 (s, 3H), 4.29 (s, 2H), 6.68 (d, J = 1.5 Hz, 1 H), 6.78 (dd, J = 8.5, 1.5 Hz, 1 H), 7.15 (d, J = 8.0 Hz , 1 H), 7.47 (t, J = 7.5 Hz, 2 H), 7.57 (t, J = 7.5 Hz, 1 H), 8.01 (d, J = 7.0 Hz, 2 H)

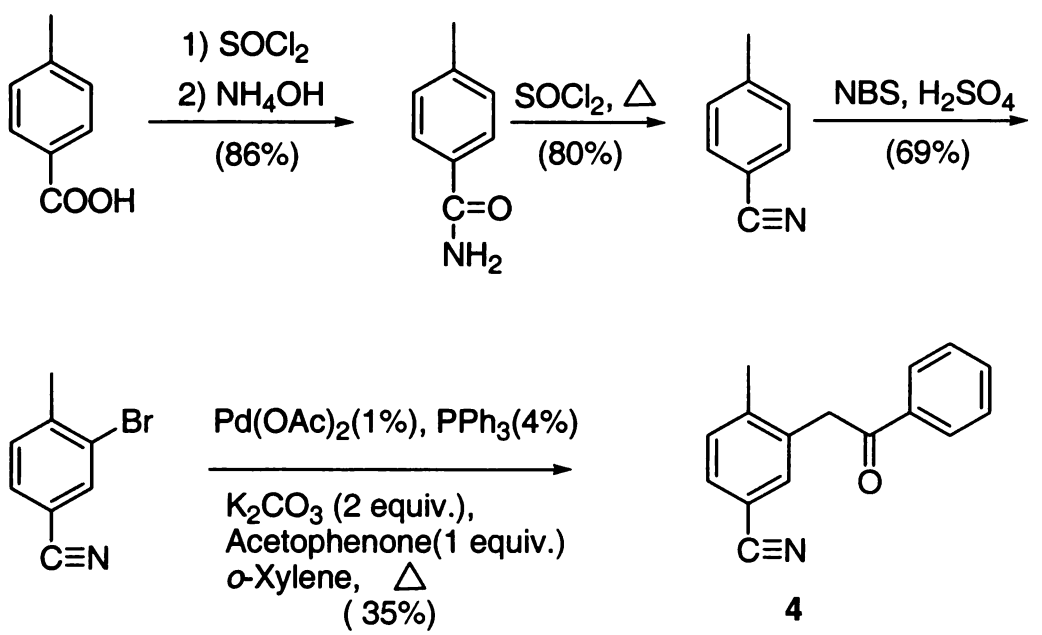
^{13}C NMR($CDCl_3$): δ 15.3, 25.5, 43.3, 55.4, 112.9, 116.4, 128.6, 128.9, 129.6, 133.4, 134.0, 134.9, 137.1, 157.9, 197.9IR (CCl_4): 1690, 1261 cm^{-1}

m.p.: 53.8-54.5 °C

Anal. Calcd for $C_{17}H_{18}O_2$:C, 80.28; H, 7.13. Found: C, 80.40; H, 7.25.

α-(5-Cyano-2-methylphenyl)acetophenone(4)

p-Toluic acid (Aldrich) was first transformed to the corresponding acyl chloride with thionyl chloride. *p*-Toluamide was then obtained by reacting the acyl chloride with aqueous ammonia (3M).[21] Dehydration of this amide furnished *p*-tolunitrile.[22] Bromination of the nitrile [23] followed by coupling with acetophenone using palladium (II) catalysis[20] gave ketone **4**.



Scheme 13. Preparation of α-(5-Cyano-2-methylphenyl)acetophenone.

p-toluamide

To a 100 mL round bottom flask equipped with a condenser, a magnetic stir bar and purged with nitrogen gas, 13.6 grams (0.1 moles) of *p*-Toluic acid was added. The flask was then heated in a water bath. When the temperature of the water bath reached 50°C, 13 mL (0.18 moles) of thionyl chloride and 20 drops of dimethylfomamide were added dropwise with stirring. Then the mixture was stirred for 15 minutes at 50-60°C until all of the acid was dissolved. The mixture was then added drop by drop into 100 mL ice-cold ammonium hydroxide (3M) with stirring. Suction filtration of the mixture afforded 11.62 grams (86% yield) of the product as white solid. This solid was used without further purification in the next step.

^{1}H NMR($CDCl_3$): δ 2.38 (s, 3 H), 5.40-6.20 (bs, 2 H), 7.23 (d, J = 7.5 Hz, 2 H), 7.68 (d, J = 8.1 Hz, 2 H)

p-tolunitrile

To a 50 mL round bottom flask equipped with a condenser, a magnetic stir bar and purged with nitrogen gas, 11.62 grams (0.086 moles) of 4-Ethylbenzamide and 30 mL of thionyl chloride were added. The mixture was refluxed for 1 hour. The excess thionyl chloride was removed by rotatory evaporator. Vacuum distillation afforded 8.07 grams of product (b.p. = 75-80°C/5mmHg) as a pale yellow oil (80% yield). This oil was used without further purification in the next step.

^{1}H NMR ($CDCl_3$): δ 2.39 (s, 3 H), 7.24 (d, *J* = 7.8 Hz,2 H), 7.51 (d, *J* = 8.1 Hz,2 H)

2-bromo-4-cyanotoluene

To a 250 mL round bottom flask equipped with a magnetic stir bar, 16.8 grams (0.143 moles) of *p*-tolunitrile and 80 mL of aqueous sulfuric acid solution (concentrated sulfuric acid :water = 1:1,v/v) were added. The flask was wrapped with aluminum foil and the reaction was allowed to run in the dark to avoid radical reactions. After the mixture was stirred for 10 minutes, 25.6 grams of N-bromo-succinimide (0.143 moles) was added to the flask slowly over 20 minutes. The mixture was stirred at room temperature for 3 days. Then the reaction mixture was extracted by ether three times. The combined ether layer was washed with brine and dried over anhydrous sodium sulfate. Solvent was removed to afford the crude product as a white solid. After silica gel chromatography (using 40:1 hexane/ethyl acetate solution as eluent), 19.44 grams (69% yield) of pure product was obtained.

^{1}H NMR ($CDCl_3$): δ 2.44 (s, 3 H), 7.30 (d, *J* = 7.8 Hz,1 H), 7.47 (dd, *J* = 8.0, 1.5 Hz, 1 H), 7.78 (d, *J* = 1.5 Hz, 1 H)

α-(5-Cyano-2-methylphenyl)acetophenone

To a 250 mL three-necked round bottom flask equipped with a thermometer, a condenser, a magnetic stir bar and purged with nitrogen gas, 0.135 grams (0.0006 moles) of palladium (II) acetate, 0.630 grams (0.0024 moles) of

triphenylphosphine and 16.6 grams (0.12 moles) of potassium carbonate was added. Then 80 mL of o-xylene was added by syringe. With stirring, 11.82 grams (0.06 moles) of 2-bromo-4-cyanotoluene dissolved in 20 mL of o-xylene was added by syringe, followed by 7.21 grams (0.06 moles) of acetophenone. The mixture was refluxed for 12 days. Then the reaction mixture was extracted by ether three times. The combined ether layer was washed with brine and dried over anhydrous sodium sulfate. Solvent was then removed to afford a yellow oil. Analysis of the oil showed it to contain the desired product and the starting materials. After silica gel chromatography (using 10:1 hexane/ethyl acetate solution as eluent), 1.60 grams of the product was obtained (35% yield, based on recovery) together with recovery of 7.98 grams of the starting bromide.

^{1}H NMR($CDCl_3$): δ 2.28 (s, 3 H), 4.33 (s, 2 H), 7.29 (d, J = 7.5 Hz, 1 H), 7.40 (s, 1 H), 7.46 to 7.52 (m, 3 H), 7.61 (t, J = 7.5 Hz, 1 H), 7.99 to 8.03 (m, 2 H)

^{13}C NMR($CDCl_3$): δ 19.8, 42.6, 109.6, 118.6, 127.9, 128.5, 130.6, 130.7, 133.4, 133.6, 134.6, 136.0, 142.8, 195.6

IR (CCl_4): 2227, 1685 cm^{-1}

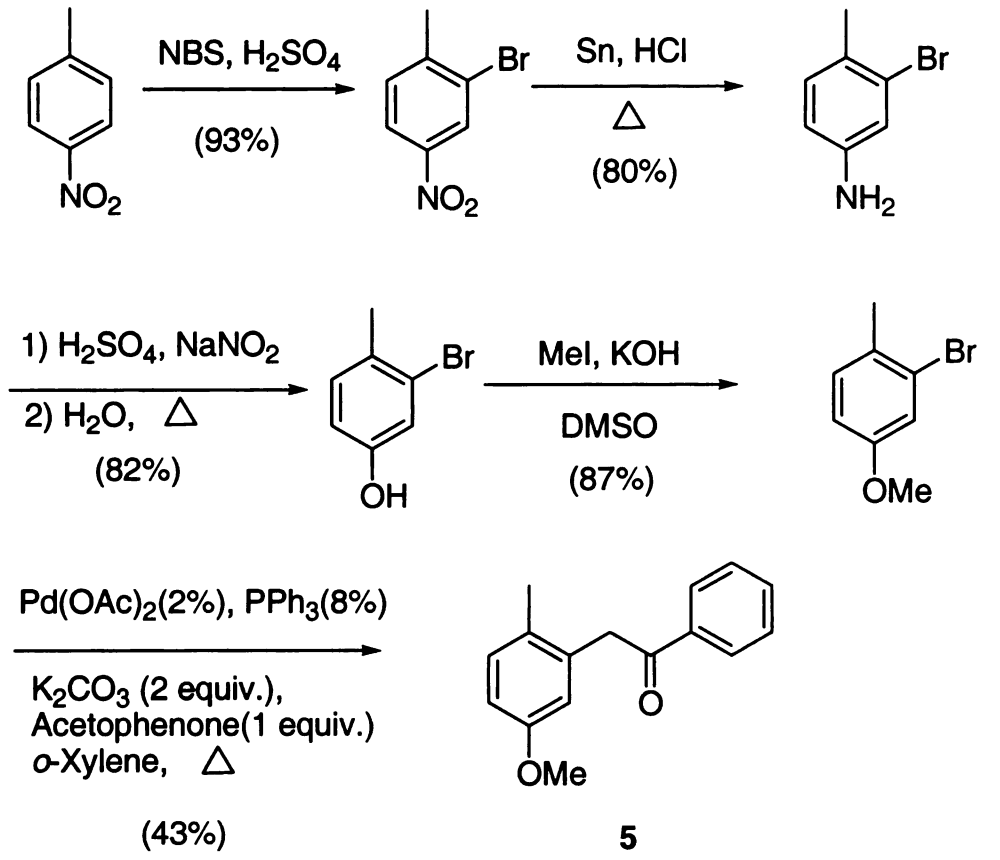
m.p.: 116.4-117.3 °C

Anal. Calcd for $C_{16}H_{13}NO_2$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.12; H, 5.48; N, 5.91.

α-(2-Methyl-5-methoxyphenyl)acetophenone (5)

p-Nitrotoluene (Aldrich) was brominated by NBS in concentrated sulfuric acid. [23] Reduction of 2-bromo-4-nitrotoluene [24] formed the corresponding aniline, which

was then taken in a Sandmeyer reaction to give 3-bromo-4-methyl-phenol.[25] Methylation of the phenol with potassium hydroxide and methyl iodide afforded 3-bromo-4-methyl-anisole,[26] which was then coupled with acetophenone using palladium (II) catalysis [20] to furnish ketone **5.**



Scheme 14. Preparation of α-(2-Methyl-5-methoxyphenyl)acetophenone.

2-bromo-4-nitrotoluene

To a 250 mL round bottom flask equipped with a magnetic stir bar, 10.0 grams (0.073 moles) of *p*-Nitrotoluene and 80 mL of aqueous sulfuric acid solution (concentrated sulfuric acid :water = 1:1,v/v) were added. The flask was wrapped with aluminum foil and the reaction was allowed to run in the dark to avoid radical

reactions. After the mixture was stirred for 10 minutes, 13.0 grams of N-bromo-succinimide (0.073 moles) was added to the flask slowly over 20 minutes. The mixture was stirred at room temperature for 24 hours. Then the reaction mixture was extracted by ether three times. The combined ether layer was washed with brine and dried over anhydrous sodium sulfate. Solvent was removed to afford 14.66 grams (93% yield) of the product as a yellow solid.

^{1}H NMR ($CDCl_3$): δ 2.48 (s, 3 H), 7.38 (d, J = 8.4 Hz, 1 H), 8.04 (dd, J = 8.3, 2.4 Hz, 1 H), 8.37 (d, J = 2.4 Hz, 1 H)

3-bromo-4-methyl-aniline

To a 100 mL three-necked round bottom flask equipped with a thermometer, a condenser, a magnetic stir bar and purged with nitrogen gas, 9.69 grams (0.0816 moles) of finely divided tin powder and 7.95 grams (0.0368 moles) of 2-bromo-4-nitrotoluene was added. The flask was cooled by an ice-water bath while 25 mL of concentrated hydrochloric acid was added dropwise with stirring. The rate of acid addition was controlled so that the temperature was maintained below 60 °C. After the initial exothermic portion of the reaction was complete, the ice water bath was removed and the reaction mixture was refluxed for 1 hour. After the mixture cooled down to room temperature, 20 M aqueous NaOH solution was added to make it basic. The organic layer was extracted by ether three times. The combined ether layer was washed with brine and dried over anhydrous sodium sulfate. Solvent was then removed to afford 5.48 grams (80% yield) of the product as a yellow oil.

^{1}H NMR($CDCl_3$): δ 2.28 (s, 3 H), 3.5-3.6 (bs, 2H), 6.52 (dd, J = 8.1, 2.4 Hz, 1 H), 6.88 (d, J = 2.1 Hz, 1 H), 6.98 (d, J = 8.1 Hz, 1 H)

3-bromo-4-methyl-phenol

To a 250 mL three-necked round bottom flask equipped with a thermometer, a magnetic stir bar and purged with nitrogen gas, 5.48 grams (0.0295 moles) of 3-bromo-4-methyl-aniline was added. To it was added the hot diluted acid obtained by adding 6 mL of concentrated sulfuric acid into 15 mL of water. The clear solution was stirred and cooled to 15°C. Then 10 grams of ice was added. As soon as the temperature had dropped below 5°C, a solution of 2.42 grams (0.035 moles) of sodium nitrite in 7 mL of water was added from a syringe, the needle of which extended below the surface of the liquid. The temperature of the solution was kept below 5°C during addition. The solution was stirred for 5 minutes after addition. Then 6 mL of cold water, 0.24 grams of urea and 15 grams of cracked ice were added successively. The solution was kept in an ice water bath until used. To another 250 mL three-necked round bottom flask equipped with a condenser, a magnetic stir bar and purged with nitrogen gas, 11.2 grams of anhydrous sodium sulfate, 15 mL of concentrated sulfuric acid and 7.5 mL of water were added. The mixture was boiled, then the solution of diazonium salt was added in portions. The mixture was refluxed for 2 hours. After cooled down to room temperature, the reaction mixture was extracted with two100 mL portions of ether, and the combined extracts were washed successively with 100 mL of water and 100 mL of 10% sodium bicarbonate solution. The phenol was then

extracted from the ether layer with one 100 mL and two 50 mL portions of 10% NaOH solution. The combined alkaline solutions were acidified, with cooling, by the addition of 100 mL of concentrated hydrochloric acid. The phenol was then extracted with one 100 mL and two 50 mL portions of ether. The combined ether layer was washed with brine and dried over anhydrous sodium sulfate. Solvent was then removed to afford 4.50 grams (82% yield) of the product as a brownish red oil.

^{1}H NMR($CDCl_3$): δ 2.28 (s, 3 H), 6.68 (dd, J = 8.4, 2.7 Hz, 1 H), 7.04 (d, J = 2.4 Hz, 1 H), 7.05 (d, J = 8.1 Hz, 1 H)

3-bromo-4-methoxytoluene

To a 100 mL round bottom flask equipped with a magnetic stir bar and purged with nitrogen gas, 5.39 grams (0.096 moles) of powdered potassium hydroxide and 50 mL of dimethyl sulfoxide were added. After stirring for 5 minutes, 4.5 grams (0.024 moles) of 3-bromo-4-methyl-phenol was added, followed immediately by 6.83 grams (0.048 moles) of methyl iodide. Stirring was continued for 4 hours. Then the mixture was poured into 200 mL of water and extracted three times with 200 mL portions of dichloromethane. The combined organic extracts were washed with brine and dried over anhydrous sodium sulfate. Solvent was then removed to afford 4.23 grams (87% yield) of product as a brownish red oil.

^{1}H NMR($CDCl_3$): δ 2.31 (s, 3 H), 3.76 (s, 3 H), 6.75 (dd, J = 8.3, 2.4 Hz, 1 H), 7.08-7.12 (m, 2 H)

α-(2-Methyl-5-methoxyphenyl)acetophenone

To a 100 mL three-necked round bottom flask equipped with a thermometer, a condenser, a magnetic stir bar and purged with nitrogen gas, 0.081 grams (0.00036 moles) of palladium (II) acetate, 0.38 grams (0.0014 moles) of triphenylphosphine and 4.95 grams (0.036 moles) of potassium carbonate was added. Then 30mL of o-xylene was added by syringe. With stirring, 3.6 grams (0.018 moles) of 3-bromo-4-methoxytoluene dissolved in 5 mL of oxylene was added by syringe, followed by 2.15 grams (0.018 moles) of acetophenone. The mixture was refluxed for 3 days. Then the reaction mixture was extracted by ether three times. The combined ether layer was washed by brine and dried over anhydrous sodium sulfate. Solvent was then removed to afford a yellow oil. Analysis of the oil showed it to contain the desired product and the starting materials. After silica gel chromatography (using 20:1 hexane/ethyl acetate solution as eluent), 1.70 grams (43% yield) of the product was obtained.

^{1}H NMR($CDCl_3$): δ 2.18 (s, 3 H), 3.74 (s, 3 H), 4.25 (s, 2 H), 6.68 (d, J = 2.5 Hz, 1 H), 6.73 (dd, J = 8.5, 2.5 Hz, 1 H), 7.10 (d, J = 8.0 Hz, 1 H), 7.44-7.46 (m, 2 H), 7.56 (t, J = 7.5 Hz, 1 H), 8.00 (d, J = 7.0 Hz, 2 H)

^{13}C NMR($CDCl_3$): δ 19.0, 43.8, 55.4, 112.5, 116.2, 128.5, 128.8, 129.0, 131.3, 133.4, 134.6, 137.0, 158.0, 197.5

IR (CCl_4): 1688 cm^{-1}

m.p.: 68.4-70.1 °C

Anal. Calcd for $C_{16}H_{16}O_2$:C, 79.97; H, 6.71. Found: C, 79.64; H, 6.52

III. Photochemical Experiments and Procedures

A. Purification of Chemicals

1. Solvent

1.5 liter of reagent grade benzene was mixed with 0.2 liter of concentrated sulfuric acid and the mixture was stirred for 2 days. The benzene layer was separated and was washed with 100 mL portions of concentrated sulfuric acid several times until the sulfuric acid layer did not turn yellow. The benzene was then washed with distilled water and saturated sodium bicarbonate solution. The benzene was separated, dried over anhydrous sodium sulfate and filtered into a 2 liter round bottom flask. Phosphorous pentoxide (50 grams) was added and the solution was reflux for 2 days. After refluxing, the benzene was distilled through a one meter column. The first and last 10% were discarded. (b.p.: 78°C)

2. Internal Standard

Eicosane(C_{20}) was purified by recrystallization from methanol.

B. Equipment and Procedures

1. Glassware

All photolysis glassware (Pyrex culture tubes, syringes, volumetric flasks, etc.) were rinsed with reagent grade acetone and distilled water and boiled in a

solution of Alconox laboratory detergent in distilled water for 2 days. They were rinsed with water and boiled in distilled water for another 2 days. After a final rinse with distilled water, the glassware was oven dried overnight and cooled to room temperature before use.

Tubes used for irradiation were made from 13×100 mm Pyrex culture tubes by flame heating them approximately 2 cm from the top with an oxygen-natural gas torch and drawing them into a uniform 15 cm length.

2. Sample Preparations

All solutions were prepared by directly weighing the desired material into volumetric flasks or by dilution of stock solutions. Equal volumes (2.8 mL) of sample were placed via syringes into each tube

3. Degassing Procedure

Irradiation tubes were attached to a vacuum line. The tubes were degassed by three consecutive freeze-pump-thaw cycles. The tubes were then sealed with an oxygen-natural gas torch while still under vacuum.

4. Irradiation Procedures

Small scale irradiations were made by irradiating 0.1 M degassed solutions of the sample in NMR tubes. A medium pressure mercury arc lamp served as the light source. The light from the source was filtered through a Pyrex glass.

C. Identification of Photoproducts

1. Products From α-(5-Cyano-2-ethylphenyl)acetophenone (2)

0.1 M solution of α-(5-Cyano-2-ethylphenyl)acetophenone in 0.7 mL of benzene-d_6 was irradiated through Pyrex filter ($\lambda > 290$ nm) at room temperature for 12 hours. The signals of two products were detectable by NMR. The effect of temperature on product ratios was studied by doing the photochemistry in ice-water, water, and silica oil baths. The diasteromeric ratio of the products were determined by NMR integration of the methyl doublet signals corresponding to each isomer. Large scale irradiation using 0.3 grams of α-(5-Cyano-2-ethylphenyl)acetophenone in 100 mL of benzene was performed until no trace of starting material could be observed by NMR. The product mixture was then separated by silica gel chromatography (using 20:1 hexane/ethyl acetate solution as eluent) to get two indanols. The Z-indanol was eluted before the E-indanol. The products were recovered as solids.

(*Z*)-5-cyano-1-methyl-2-phenyl-indan-2-ol

^{1}H NMR ($CDCl_3$) δ 1.27 (d, J =7.0 Hz, 3 H), 3.19, 3.48 (AB quartet, J = 16.8 Hz, 2 H), 3.58 (quartet, J = 7.5 Hz, 1H), 7.27-7.32 (m, 2 H), 7.39 (t, J =7.0 Hz, 2 H), 7.51-7.58 (m, 4 H);

^{1}H NMR (Benzene-d_6) δ 0.95 (d, J =6.9 Hz, 3 H), 2.64, 2.95 (AB quartet, J = 16.6 Hz, 2 H), 3.03 (quartet, J = 6.6 Hz, 1H), 6.61 (d, J =7.8 Hz, 1 H), 6.84 (s, 1 H), 7.21-7.40 (m, 3 H), 8.07-8.10 (m, 3 H). A doublet (J = 7.2 Hz),

^{13}C NMR ($CDCl_3$) δ 10.3, 48.9, 50.7, 85.6, 110.9, 119.6, 124.6, 125.5, 127.7, 128.4, 128.7, 131.7, 141.9, 143.7, 151.3

m.p. 99.9-101.4 °C

IR (CCl_4) 3476, 2228 cm^{-1}

MS (FAB) m/z 250.1233 (MH^+).

(*E*)-5-cyano-1-methyl-2-phenyl-indan-2-ol

^1H NMR ($CDCl_3$) δ 0.80 (d, *J* =8.0 Hz, 3 H), 3.20, 3.79 (AB quartet, *J* = 16.5 Hz, 2 H), 3.46 (quartet, *J* = 7.5 Hz, 1H), 7.28-7.43 (m, 6 H), 7.52 (d, *J* =8.0 Hz, 1 H), 7.58 (s, 1H)

^{13}C NMR ($CDCl_3$) δ 17.0, 43.6, 52.0, 85.6, 110.2, 119.1, 124.7, 125.7, 127.5, 128.0, 128.1, 131.0, 141.1, 142.2, 152.5

m.p. 103.6-105.1°C

IR (CCl_4) 3453, 2228 cm^{-1}

Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N 5.62. Found: C, 81.16; H, 5.86; N, 5.66

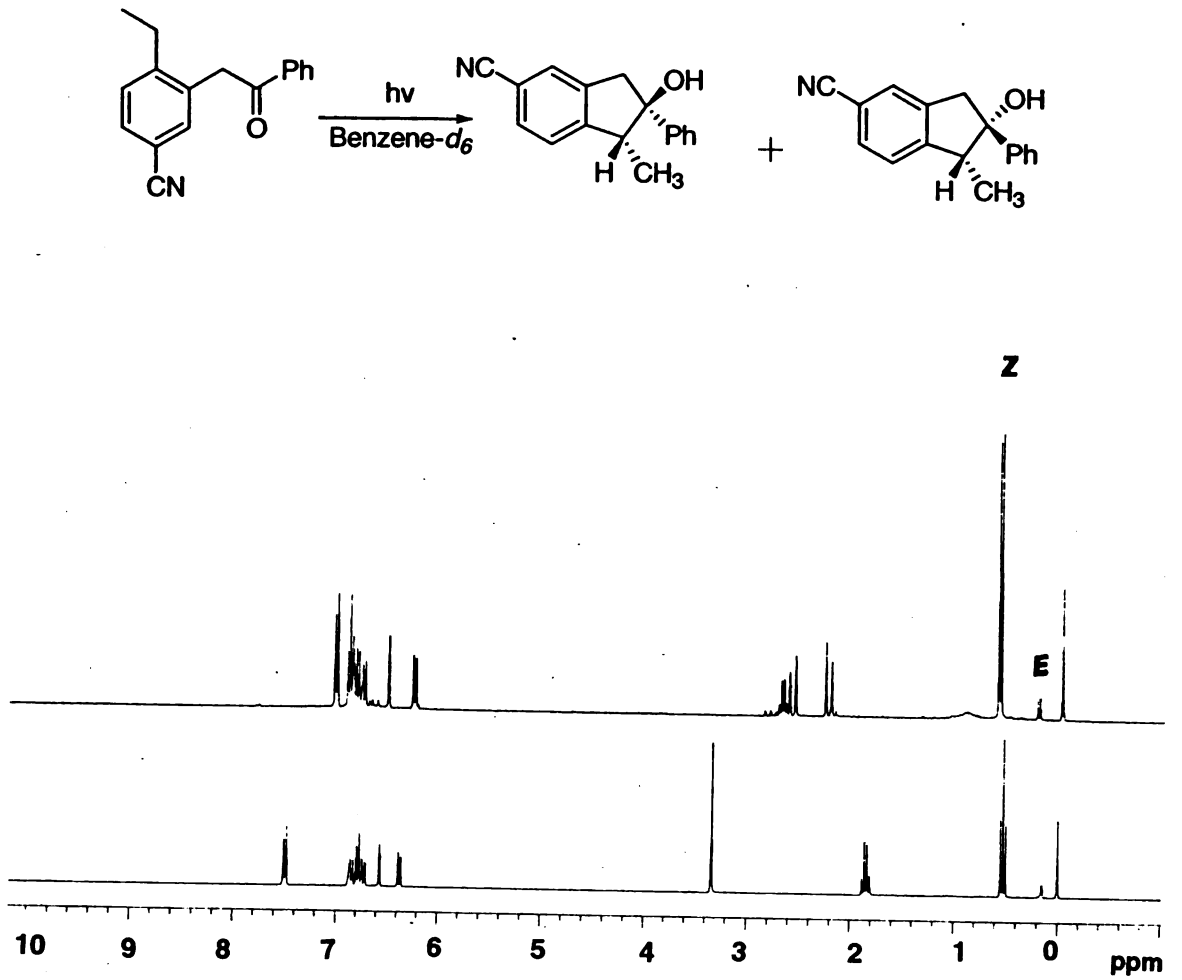


Figure 1. ^{1}H NMR of α-(5-Cyano-2-ethylphenyl)acetophenone Before and After Irradiation in Benzene-d_6 (λ> 290 nm)

2. Products From α-(2-Ethyl-5-methoxyphenyl)acetophenone (3)

0.1 M solution of α-(2-Ethyl-5-methoxyphenyl)acetophenone in 0.7 mL of benzene-d_6 was irradiated through Pyrex filter (λ > 290 nm) at room temperature for 6 hours. The signals of two products were detectable by NMR. The effect of temperature on product ratios was studied by doing the photochemistry in ice-water, water, and silica oil baths. The diasteromeric ratio of the products were determined by NMR integration of the methyl doublet signals corresponding to each isomer. Large scale irradiation using 0.3 grams of α-(2-Ethyl-5-methoxyphenyl)acetophenone in 100 mL of benzene was performed until no trace of starting material could be observed by NMR. The product mixture was then separated by silica gel chromatography (using 20:1 hexane/ethyl acetate solution as eluent) to get two indanols. The Z-indanol was eluted before the E-indanol. The products were recovered as solids.

(Z)-5-methoxy-1-methyl-2-phenyl-indan-2-ol

^{1}H NMR ($CDCl_3$) δ 1.21 (d, *J* =6.9 Hz, 3 H), 3.11, 3.48 (AB quartet, *J* = 16.8 Hz, 2 H), 3.51 (quartet, *J* = 7.5 Hz, 1H), 3.80 (s, 3 H), 6.78-6.82 (m, 2 H), 7.09 (d, *J* =8.1 Hz, 1 H), 7.28-7.41 (m, 3 H), 7.60 (d, *J* = 7.8 Hz, 2 H)

^{1}H NMR (Benzene-d_6) δ 1.11 (d, *J* = 7.2 Hz, 3 H), 2.90, 3.27 (AB quartet, *J* = 16.6 Hz, 2 H), 3.30 (quartet, *J* = 7.2 Hz, 1H), 3.73 (s, 3 H), 6.71 (s, 1 H), 6.79 (dd, *J* = 2.7, 8.4 Hz, 1 H), 6.93 (d, *J* = 7.8 Hz, 1 H), 7.18-7.24 (m, 2 H), 7.51-7.55 (m, 2 H), 8.07-8.11 (m, 1 H)

^{13}C NMR ($CDCl_3$) δ 10.9, 49.6, 50.0, 55.7, 85.8, 111.0, 112.9, 124.6, 125.6, 127.2, 128.4, 137.4, 141.8, 144.4, 159.5

m.p. 49.3-50.5 °C

IR (CCl_4) 3492, 1248 cm^{-1}

Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.45; H, 7.22

(E)-5-methoxy-1-methyl-2-phenyl-indan-2-ol

^1H NMR ($CDCl_3$) δ 0.77 (d, *J* =7.2 Hz, 3 H), 3.15, 3.73 (AB quartet, *J* = 16.2 Hz, 2 H), 3.35 (quartet, *J* = 7.2 Hz, 1H), 3.80 (s, 3 H), 6.76 (d, *J* = 8.7 Hz, 1H), 6.87 (s, 1 H), 7.10 (d, *J* = 7.8 Hz, 2 H), 7.27-7.45 (m, 4 H)

^{13}C NMR ($CDCl_3$) δ 18.0, 45.1, 51.9, 55.7, 86.7, 110.8, 112.9, 125.2, 126.4, 127.6, 128.4, 139.1, 141.7, 143.4, 159.3

m.p. 52.9-53.6 °C

IR (CCl_4) 3427, 1249 cm^{-1}

Anal. Calcd for $C_{17}H_{18}O_2$:C, 80.28; H, 7.13. Found: C, 80.57; H, 7.34

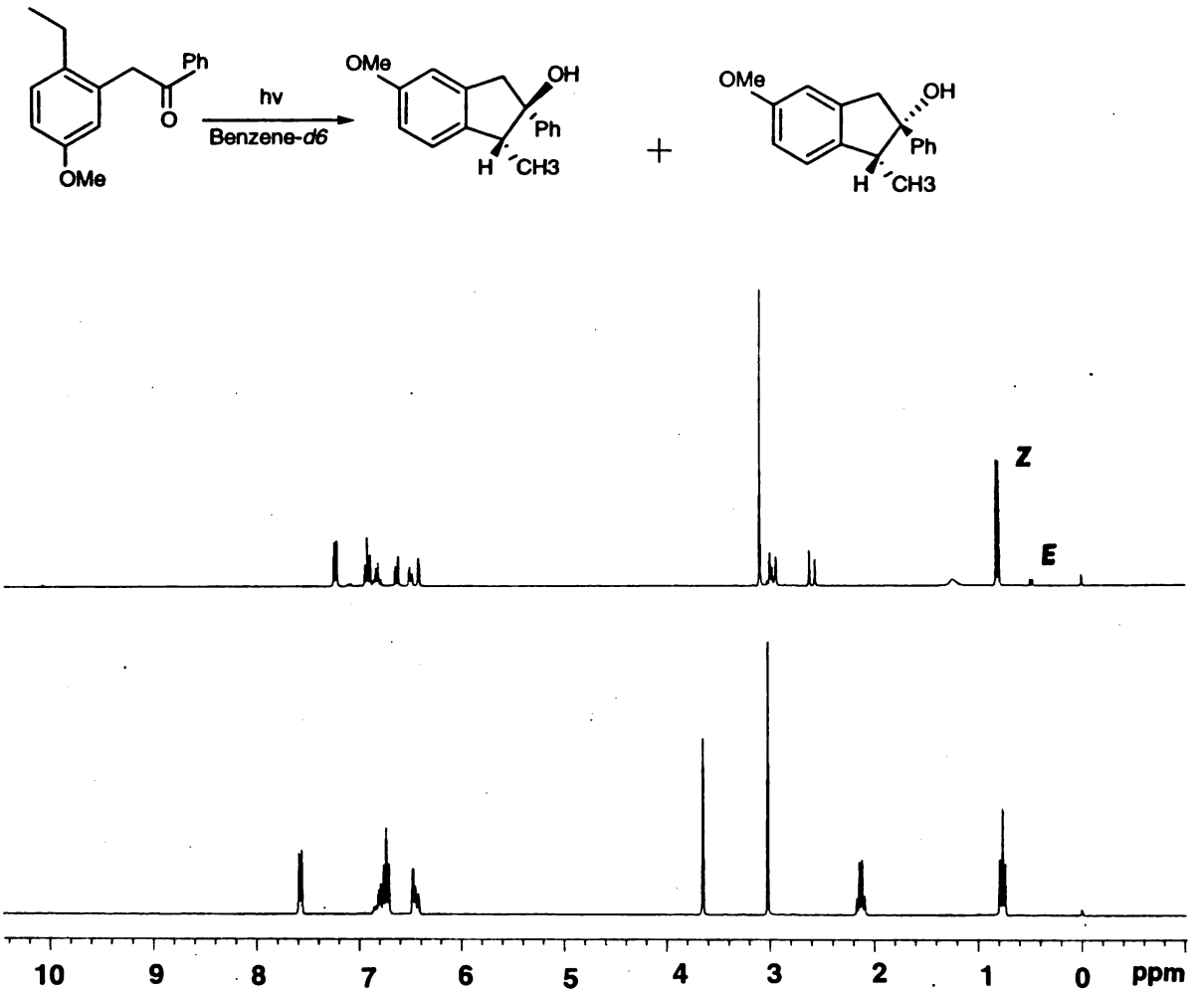


Figure2. ^{1}H NMR of α-(2-Ethyl-5-methoxyphenyl)acetophenone Before and After Irradiation in Benzene-d_6 (λ> 290 nm)

3. Product From α-(5-Cyano-2-methylphenyl)acetophenone(4)

0.1 M solution of α-(5-cyano-2-methylphenyl)acetophenone in 0.7 mL of benzene-d_6 was irradiated through Pyrex filter ($\lambda > 290$ nm) at room temperature. Only one photoproduct was observed in both ^1H NMR and GC spectrum, and the reaction completed within 5 hours. Large scale irradiation using 0.3 grams of α-(5-Cyano-2-methylphenyl)acetophenone in 100 mL of benzene was performed until no trace of starting material could be observed by NMR. The product was then purified by silica gel chromatography (using 10:1 hexane/ethyl acetate solution as eluent).

5-Cyano-2-phenyl-indan-2-ol

^1H NMR ($CDCl_3$) δ 2.22 (br s, 1 H), 3.29, 3.50 (AB quartet, J = 16.2 Hz, 4 H), 7.30-7.40 (m, 4 H), 7.46-7.54 (m, 4 H)

^{13}C NMR ($CDCl_3$) δ 48.1, 48.6, 82.9, 110.1, 119.2, 124.8, 125.3, 127.3, 128.0, 128.2, 130.8, 142.2, 144.4, 146.8

IR (CCl_4) 3458, 2228 cm^{-1}

m.p.: 123.6-124.3 °C

Anal. Calcd for $C_{16}H_{13}NO_2$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.08; H, 5.44; N, 5.90

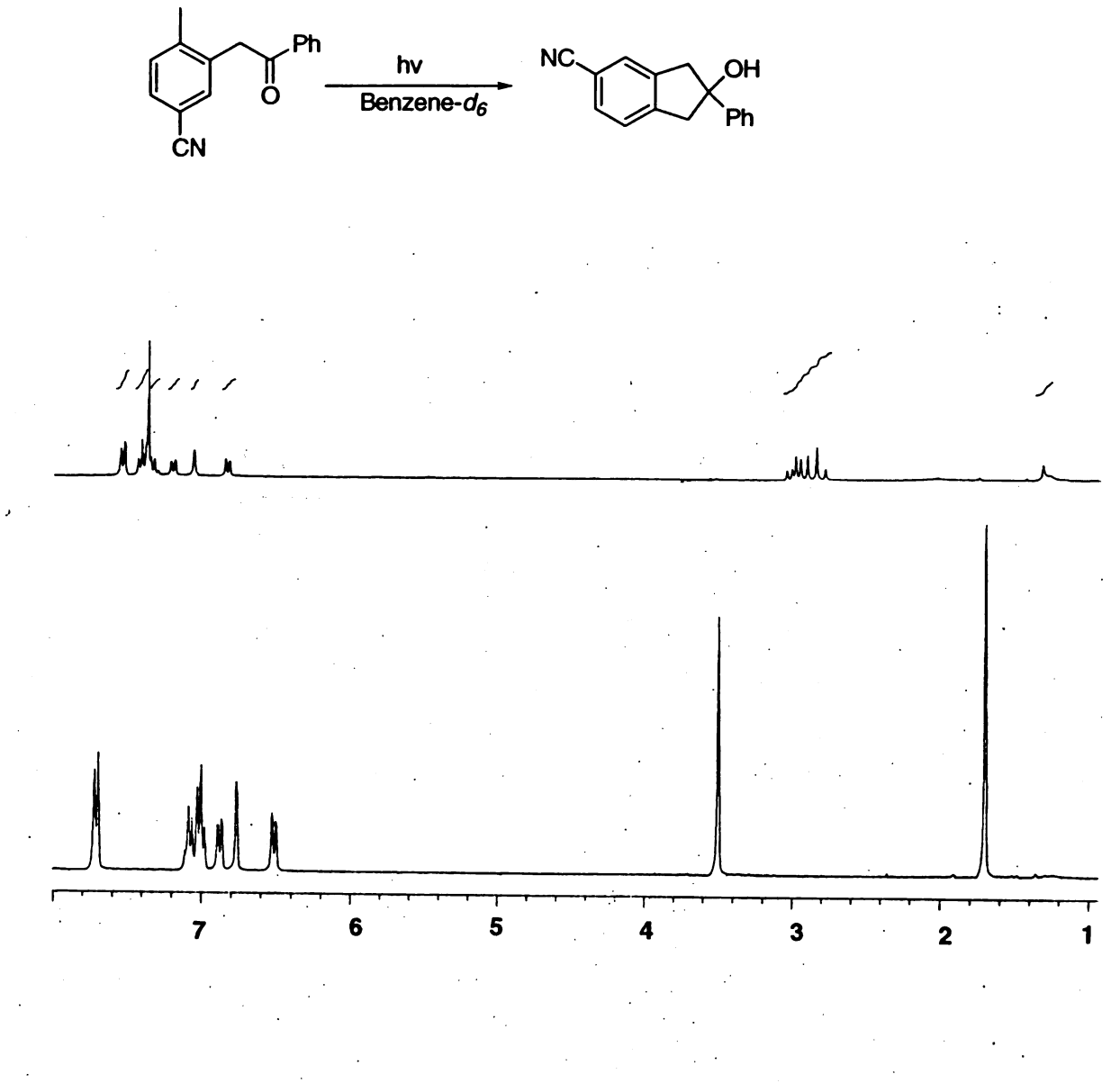


Figure 3. ^{1}H NMR of α-(5-Cyano-2-methylphenyl)acetophenone Before and After Irradiation in Benzene-d_6 (λ> 290 nm)

4. Products From α-(2-Methyl-5-methoxyphenyl)acetophenone(5)

0.1 M solution of α-(2-Methyl-5-methoxyphenyl)acetophenone in 0.7 mL of benzene-d_6 was irradiated through Pyrex filter (λ > 290 nm) at room temperature. Only one photoproduct was observed in both ^{1}H NMR and GC spectrum, and the reaction completed within 3 hours. Large scale irradiation using 0.3 grams of α-(2-Methyl-5-methoxyphenyl)acetophenone in 100 mL of benzene was performed until no trace of starting material could be observed by NMR. The product was then purified by silica gel chromatography (using 10:1 hexane/ethyl acetate solution as eluent).

5-Methoxy-2-phenyl-indan-2-ol

^{1}H NMR (benzene-d_6) δ 2.96, 3.21 (AB quartet, J = 15.8 Hz, 4 H), 3.34 (s, 3 H), 6.69 (s, 1 H), 6.73 (dd, J = 2.5, 8.0 Hz, 1 H), 6.92 (d, J = 8.5 Hz, 1 H), 7.05-7.17 (m, 3 H), 7.42-7.44 (m, 2 H)

^{13}C NMR (benzene-d_6) δ 49.2, 50.2, 54.8, 83.3, 110.7, 112.9, 125.3, 125.5, 126.9, 128.2, 133.3, 142.9, 146.9, 159.7

IR (CCl_4) 3469, 1282 cm^{-1}

mp 66.5-68.1 °C

Anal. Calcd for $C_{16}H_{16}O_2$:C, 79.97; H, 6.71. Found: C, 79.58; H, 6.58

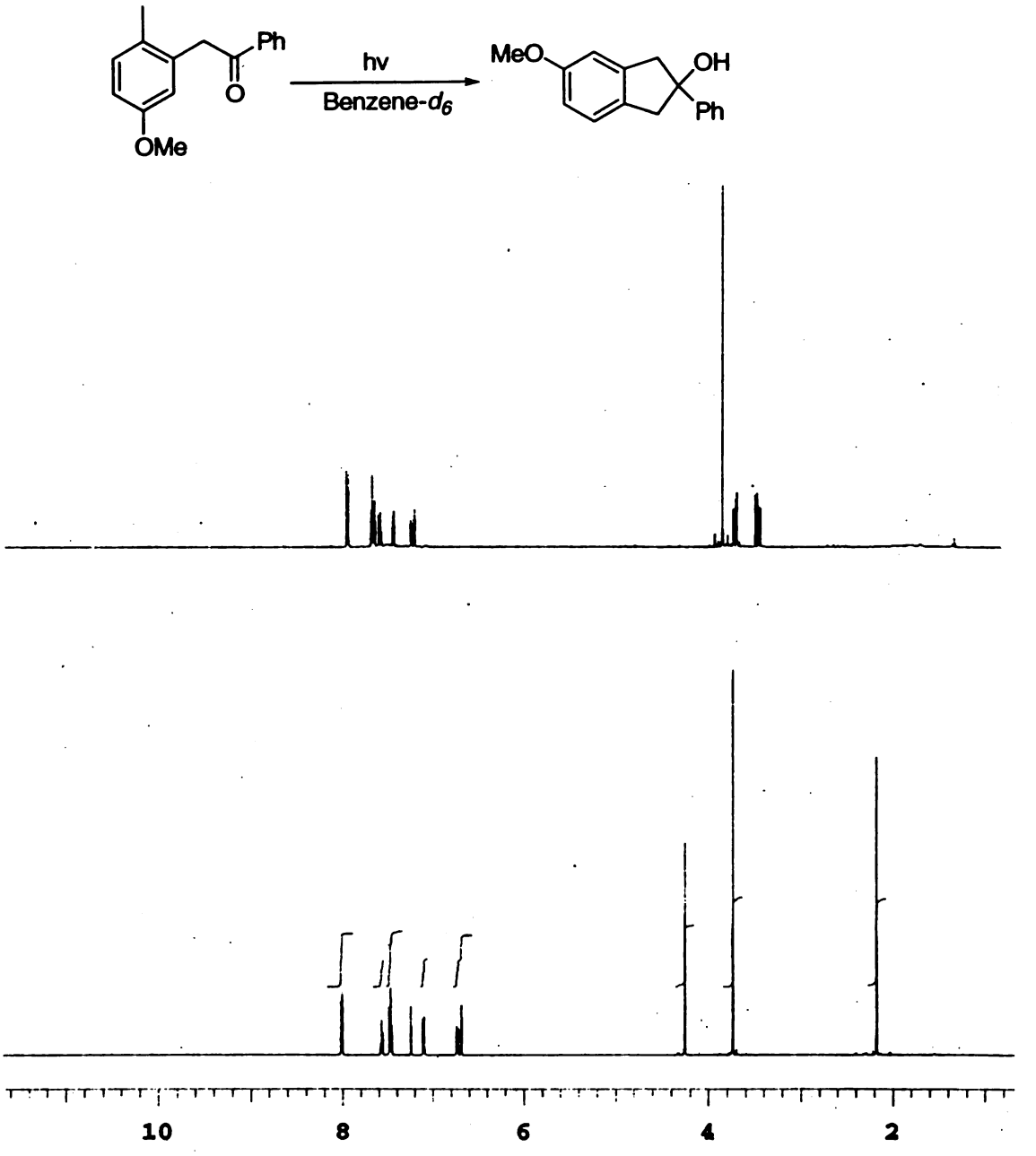


Figure 4. ^{1}H NMR of α-(2-Methyl-5-methoxyphenyl)acetophenone Before and After Irradiation in Benzene-d_6 (λ> 290 nm)

D. Quantitative Measurements

1. Quanntum Yield Measurements

Quantum yields for cyclization product formation were measured by irradiating solutions of desired precursor parallel to 0.01 M valerophenone samples in sealed, degassed tubes. Quantum yields were calculated from the following equation, [27]

$$\Phi \overset{\text{def}}{=\!=} \frac{\text{Number of molecules of product produced}}{\text{Number of photons of light absorbed}} = [PP] / I$$

Equation 1

where [PP] is the concentration of photoproduct and I is the intensity of light absorbed by the sample.

The value of I was determined by 0.01 M valerophenone actinometer irradiated parallel with the samples to be analyzed. The irradiation was stopped after less than 10% conversion of valerophenone and the sample was analyzed for presence of acetophenone. Acetophenone's concentration was then determined from Equation 2:

$$[AP] = R_f \times [Std] \times A_{AP} / A_{std}$$

Equation 2

where [AP] is the concentration of acetophenone, R_f is the instrument response factor for acetophenone, A_{Ap} is the integrated area for acetophenone, [Std] is the concentration of internal standard, and A_{std} is the integrated area for internal standard. The intensity of the light, I, can then be calculated using the

acetophenone concentration base on $\Phi_{AP} = 0.33$ (when λ=313nm in benzene solution), [15] thus,

$$I = [AP] / 0.33$$

The concentration of photoproduct, [PP], can be calculated using Equation 3.

$$[PP] = R_{f(PP)} \times [Std] \times A_{PP} / A_{std}$$

Equation 3

Where $R_{f(PP)}$ is the instrument response factor for the photoproduct and A_{PP} is the integrated area for the photoproduct. The instrument response factor for the photoproduct were obtained using equation 4:

$$R_{f(PP)} = ([PP]/[Std]) \times (A_{std} / A_{PP})$$

Equation 4

2. Quenching Studies

Stern-Volmer quenching studies were performed by irradiating sealed degassed tubes containing the ketone and various amounts of quencher (2,5-dimethyl-2,4-hexadiene). The quenching is assumed to be diffusion-controlled with a rate constant equals to $6 \times 10^{9} M^{-1} S^{-1}$. [18] The results of these experiments are summarized below.

Quantum Yield Measurment for α-(5-Cyano-2-ethylphenyl)acetophenone

GC analysis: VG-TRIO-1

Carrier Gas: Helium

Pressure of Carrier Gas: 7.5 Psi

Initial column temp.: 80℃

Initial col. Hold time: 2 min.

Final col. Temp.: 280℃

Rate: 15℃/min., Hold time: 2 min.

Table 8. Product Quantum Yield of α-(5-Cyano-2-ethylphenyl)acetophenone in Benzene

Photoproduct	A(product)	A(std.)	Concentration	Φ
Indanols	18309680	29293936	3.148e-4M	0.296
Indanols	28910406	49055424	2.970e-4M	0.279
Indanols	25537978	40793400	3.154e-4M	0.296
Indanols	41549092	66075024	3.169 e-4M	0.298
Indanols(avg.)				0.292±0.013

[Ketone]=1.734e-3M, ε_{313nm}=282.6, [C_{20}]=9.597e-5M, $R_f^{indanols}$=5.25

[VP] =1.000e-2M, [C_{20}] =1.092e-3M, R_f^{AP} = 4.01

Irradiation source=Mercury Arc Lamp, λ=313nm, Irradiation Time = 6hrs

Quantum Yield Measurment for α-(2-Ethyl-5-methoxyphenyl)acetophenone

GC analysis: VG-TRIO-1

Carrier Gas: Helium

Pressure of Carrier Gas: 7.5 Psi.

Initial column temp.: 80℃

Initial col. Hold time: 2 min.

Final col. Temp.: 280℃

Rate: 15℃/min., Hold time: 2 min.

Table 9. Product Quantum Yield of α-(2-Ethyl-5-methoxyphenyl)acetophenone in Benzene

Photoproduct	A(product)	A(std.)	Concentration	Φ
Indanols	8228722	1380540416	2.468e-4M	0.595
Indanols	7543025	1279699840	2.440e-4M	0.588
Indanols	4547281	738286208	2.550e-4M	0.614
Indanols	7147236	1176859264	2.514e-4M	0.606
Avg.				0.601±0.013

[Ketone]=2.402e-3M, ε_{313nm}=208.9, [C_{20}]=1.270e-2M, $R_f^{indanols}$=3.26

[VP] =1.031e-2M, [C_{20}]=1.971e-3M, R_f^{AP} = 4.01

Irradiation source=Mercury Arc Lamp, λ=313nm, Irradiation Time = 3hrs.

Quantum Yield Measurment for α-(5-cyano-2-methylphenyl)acetophenone

GC analysis: VG-TRIO-1

Carrier Gas: Helium

Pressure of Carrier Gas: 7.5 Psi.

Initial column temp.: 80℃

Initial col. Hold time: 2 min.

Final col. Temp.: 280℃

Rate: 15℃/min., Hold time: 2 min.

Table 10. Product Quantum Yield of α-(5-cyano-2-methylphenyl)acetophenone in Benzene

Photoproduct	A(product)	A(std.)	Concentration	Φ
Indanols	9283746	24575364	2.292e-4M	0.340
Indanols	21464002	56255476	2.315e-4M	0.343
Indanols	23432908	61783584	2.301e-4M	0.341
Indanols	17551224	46114864	2.309e-4M	0.342
Indanols(avg.)				0.342±0.002

[Ketone]=2.094e-3M, ε_{313nm}=243.5, [C_{20}]=9.928e-5M, $R_f^{indanols}$=6.11

[VP] =1.037e-2M, [C_{20}]=1.234e-3M, R_f^{AP} = 4.01

Irradiation source=Mercury Arc Lamp, λ=313nm, Irradiation Time = 4hrs

Quantum Yield Measurment for α-(5-methoxy-2-methylphenyl)acetophenone

GC analysis: VG-TRIO-1

Carrier Gas: Helium

Pressure of Carrier Gas: 7.5 Psi.

Initial column temp.: 80℃

Initial col. Hold time: 2 min.

Final col. Temp.: 280℃

Rate: 15℃/min., Hold time: 2 min.

Table 11. Product Quantum Yield of α-(5-methoxy-2-methylphenyl)acetophenone in Benzene

Photoproduct	A(product)	A(std.)	Concentration	Φ
Indanols	242569008	389599712	5.468e-4M	0.973
Indanols	292571168	466273312	5.511e-4M	0.980
Indanols	139761936	220447024	5.568e-4M	0.990
Indanols	166798384	269120448	5.443e-4M	0.968
Indanols(avg.)				0.978±0.012

[Ketone]=2.650e-3M, ε_{313nm}=198.3, [C_{20}]=3.404e-4M, $R_f^{indanols}$=2.58

[VP] =1.072e-2M, [C_{20}]=8.865e-4M, R_f^{AP} = 4.01

Irradiation source=Mercury Arc Lamp, λ=313nm, Irradiation Time = 3.3hrs

Table 12. Quenching of the Indanol Formation in α-(5-Cyano-2-ethylphenyl) acetophenone

[Q]	A (Product)/A(std.)	Φ^0/Φ
0.00	0.880	1.00
0.00780	0.785	1.12
0.0304	0.619	1.42
0.0508	0.503	1.75

[Ketone]=0.064M, Quencher=2, 5-dimethyl-2, 4-hexadiene

$k_q\tau$= 14.5

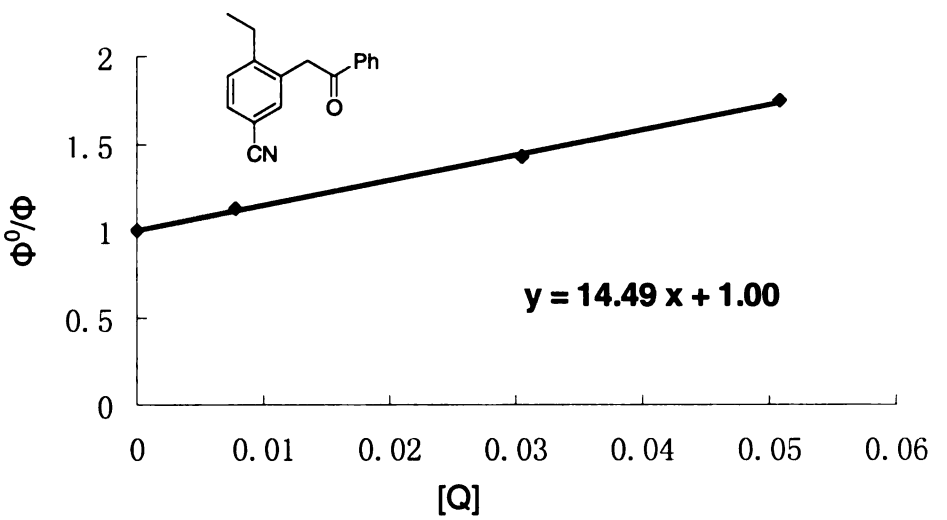


Figure 5. Stern-Volmer Plot from Quenching Study of α-(5-Cyano-2-ethylphenyl) acetophenone

Table 13. Quenching of the Indanol Formation in α-(2-Ethyl-5-methoxyphenyl) acetophenone

[Q]	A (Product)/A(std.)	Φ^0/Φ
0.00	1.500	1.00
0.0173	1.438	1.04
0.0464	1.338	1.12
0.0653	1.288	1.16

[Ketone]=0.075M, Quencher=2, 5-dimethyl-2, 4-hexadiene

kqτ= 2.54

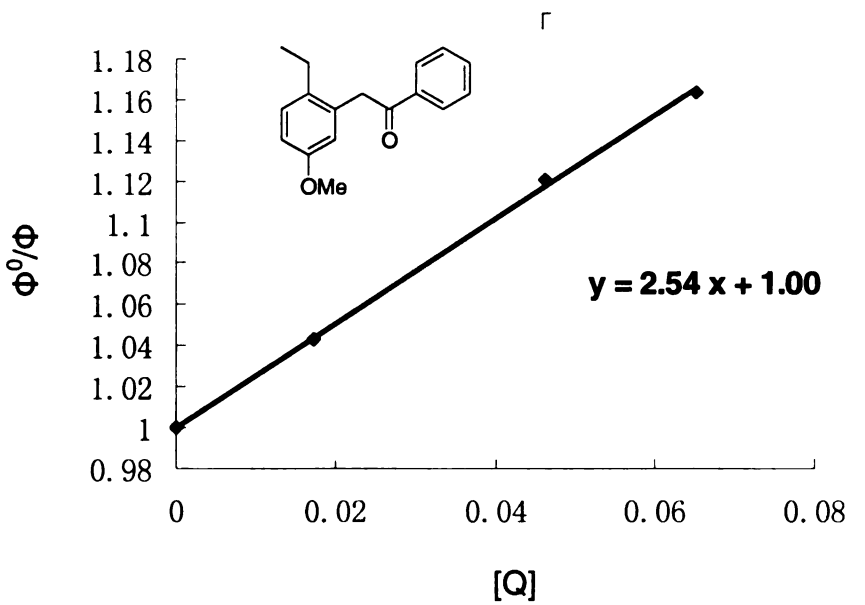


Figure 6 Stern-Volmer Plot from Quenching Study of α-(2-Ethyl-5-methoxyphenyl) acetophenone

Table 14. Quenching of the Indanol Formation in α-(5-Cyano-2-methylphenyl) acetophenone

[Q]	A (Product)/A(std.)	Φ^0/Φ
0.00	0.667	1.00
0.00944	0.439	1.52
0.0132	0.388	1.72
0.0187	0.338	1.97

[Ketone]=0.032M, Quencher=2, 5-dimethyl-2, 4-hexadiene

kqτ= 53.1

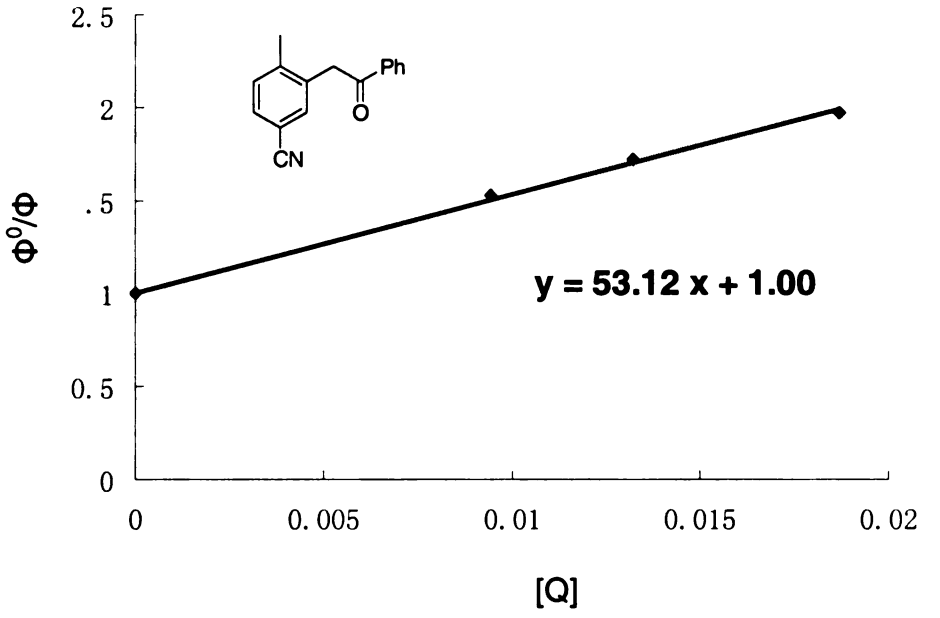


Figure 7. Stern-Volmer Plot from Quenching Study of α-(5-Cyano-2-methylphenyl) acetophenone

Table 15. Quenching of the Indanol Formation in α-((2-Methyl-5-methoxyphenyl) acetophenone

[Q]	A (Product)/A(std.)	Φ^0/Φ
0.00	0.387	1.00
0.00581	0.358	1.08
0.0198	0.296	1.31
0.0535	0.216	1.79

[Ketone]=0.068M, Quencher=2, 5-dimethyl-2, 4-hexadiene

$kq\tau = 14.9$

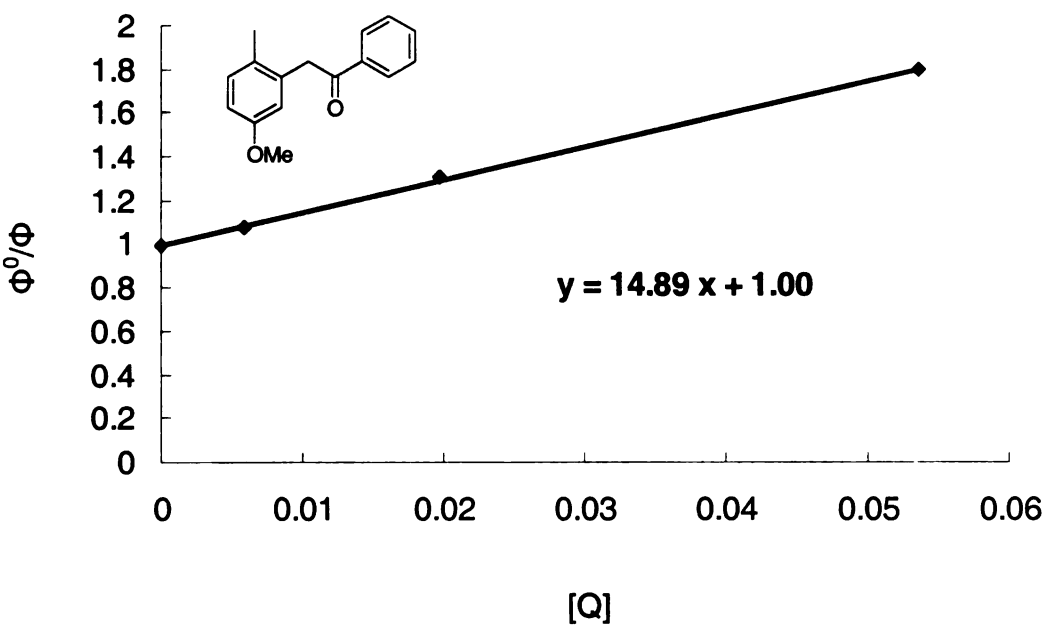


Figure 8. Stern-Volmer Plot from Quenching Study of α-(2-Methyl-5-methoxyphenyl)acetophenone

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